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Preparation and evaluation of exactly alternating silarylene-siloxane polymers.

Petar Radivoj Dvornić
University of Massachusetts Amherst

PREPARATION AND EVALUATION OF EXACTLY ALTERNATING SILARYLENE-SILOXANE POLYMERS

A Dissertation Presented

By

PETAR RADIVOJ DVORNIĆ

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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Polymer Science and Engineering

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May 1979

DEDICATION

To my Nana, Dada, Mama, Tata and Dundo for all their love, inspiration and encouragement without which I would have never come to this.

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I am ever indebted to the chairperson of the dissertation committee, my advisor during the last three and a half years, Professor Robert W. Lenz, for his whole hearted support and extremely valuable discussions throughout the research and the writing of this dissertation.

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The elemental analyses included in this work were performed by the staff of the Microanalytical Laboratory of the University of Massachusetts and I thank them for the good job they did.

Finally, my fellow graduate students did much to make the last three and a half years fun. I wish to thank them as a whole for their friendship and help.

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PREFACE

The work in this dissertation is presented in six separate chapters, each of which may be read independently of the others. The main experimental objective involved the synthesis of exactly alternating silarylene-siloxane polymers. The procedure which was developed to meet this objective is described in Chapter IV. In Chapters II and III the syntheses and properties of the monomers used in the polymerizations are discussed. All of the polymers prepared were characterized for their structural and physical properties, and these investigations are presented in Chapter V. Chapter VI is entirely devoted to the thermal degradation and thermal stability of the exactly alternating silarylene-siloxane polymers prepared. An introduction and a review of the historical developments in the field are presented in Chapter I.

ABSTRACT

Preparation and Evaluation of Exactly Alternating
Silarylene-Siloxane Polymers

(May 1979)

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Synthetic procedures for preparation of exactly alternating silarylene-siloxane polymers were developed. The condensation polymerization reactions were based on the use of arylenedisilanols and reactive bisureidosilanes as monomers. Optimization of these reactions led to the development of methods involving mild reaction conditions and relatively short reaction times for the preparation of high molecular weight polymers ($\overline{M}_w$ above 200,000). Problems involving the preparation of highly pure bisureidosilane monomers, the monitoring of the condensation polymerization reactions to prepare high molecular weight polymers, the unusually broad molecular weight distributions obtained, and the long reaction times were resolved. Preparations of monomers, polymerization procedure and methods for monitoring the reaction are described in detail.

Using the techniques developed in these investigations, twelve different homopolymers and copolymers containing exactly alternating

silarylene-siloxane structures were prepared in high molecular weight from two different arylenedisilanol monomers: 1,4-bis(dimethylhydroxysilyl)benzene and 4,4'-bis(dimethylhydroxysilyl)diphenyl ether, and two different bisureidosilane monomers: bis(1,1-tetramethylene-3-phenylureido)dimethylsilane and bis(1,1-tetramethylene-3-phenylureido)methylvinylsilane.

All of the polymers were characterized by elemental analysis, ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, IR spectroscopy, gel permeation chromatography, dilute solution viscosity and differential scanning calorimetry. The methods used and the results are described.

Thermogravimetric analysis (in air and in nitrogen) and controlled pyrolysis were used to investigate the thermal and thermo-oxidative degradation and stability of these polymers. Intermediates and products of these reactions were analyzed by elemental analysis and gas chromatography. It was observed that although different degradation mechanisms apparently operated in the two atmospheres, all of the polymers showed extremely high stability which along with their low glass transition temperatures (as determined by DSC), suggests they may be useful new technological materials.

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C H A P T E R I

A REVIEW OF THE HISTORICAL DEVELOPMENTS IN THE CHEMISTRY OF SILARYLENE-SILOXANE POLYMERS

Silicones were the first class of useful polymers based upon organometallic chemistry. Historically, their source can be traced from the nineteenth century in the work of Berzelius, Ebelman, Wöhler. Friedel and Crafts synthesized the first organosilicon compound, tetraethylsilane in 1863[1]. About half a century later the work of Frederic S. Kipping at Nottingham, England, made possible by the discovery of the Grignard reagent, established the foundations of what we now know as silicon chemistry.

During the period 1901-1945 Kipping reported in over fifty papers[2-7] the first systematic investigation directed at the elucidation of the elementary chemistry of silicon compounds. Kipping was a classical organic chemist and picked silicon for study because it was the one element most likely to have properties similar to those of carbon. He expected, for example, that the elimination of water from silanols would give the compound $Ar_2Si = O$, which by analogy with ketones he would call a "silicone." Fortunately for polymer chemistry it turned out that such hypothetical monomers could not be isolated and instead silanols always condensed to higher molecular weight Si-O-Si compounds. However, in spite of his accurate perception of

their structure[3-7], Kipping still named the products "silicones." Though they were not then considered significant, these compounds were the prototypes of today's commercially important polymers, and the term "silicones" has persisted as their trivial name.

After Kipping's discovery, it was in the United States where the intensive study of high polymer silicones really started. Hyde, Sullivan and their co-workers[8] at the Corning Glass Company (Corning, New York) synthesized in 1931 the first polymer for use with glass-fiber fabrics on high temperature electrical insulation because their thermal stability was far greater than that of the organic polymers and their dielectric properties were adequate. Shortly after, McGregor at the Mellon Institute of Industrial Research[9] obtained a series of poly(dimethylsiloxanes). However, it was not until World War II that production of the first commercial silicone began for use as an ignition-sealing compound for aircraft through the joint efforts of the Corning Glass Company and the Dow Chemical Company. This cooperation led to the creation of the Dow Chemical Corporation and to the construction of the plant for the synthesis of the monomer which was initially based upon the Grignard process.

Following shortly thereafter, Rochow[10] reported the direct synthesis of methylchlorosilanes from silicon metal and methylchloride, a process on which General Electric Company later expanded to start commercial production in 1947. A very significant contribution to the knowledge of silicon chemistry as well as polymeric

siloxanes has come from the work initiated in the Soviet Union by K. A. Andrianov which started in 1938 and developed into large scale industrial production of organosilicon polymers by 1947[26].

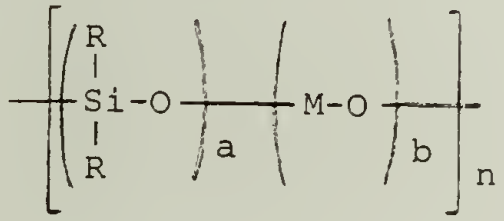
From the pioneering scientific research performed by Kipping and his followers, the fluid, resinous and elastomeric polysiloxanes, based upon macromolecular chains of alternating silicon and oxygen atoms, have found widespread use in a variety of applications because of their ability to exhibit very useful technological properties over an extremely wide temperature range. In addition to excellent chemical, mechanical and electrical properties not common to any other class of polymers, organopolysiloxanes are characterized by very low glass transition temperatures (as low as -123°C for poly(dimethylsiloxane) which is the lowest known uncontroversial glass transition temperature) which make them extraordinarily good elastomers, and thermal stabilities superior to most of the carbon-based polymers, which make them more than suitable for many high temperature applications.

Among the most desirable properties of silicon polymers in addition to high thermal and oxidative stability are high dielectric strength, low power loss, insolubility in water, relative inertness to many ionic reagents, valuable surface characteristics and useful rheological properties. The major applications of silicone polymers and fluids are in insulation, industrial paints, liquid coolants, dielectric fluids, polishes for automobiles and furniture, antifoam agents, agents for paper and textile treatment, gaskets and seals, electrical wire and cable insulation, medical uses, materials for

encapsulating, mold-forming and general sealing operations[27].

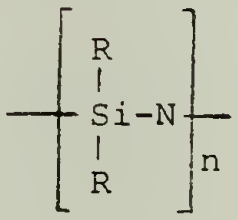
Nevertheless, even such excellent materials as polysiloxanes do have certain deficiencies, the most prominent being low tensile strength and abrasion resistance. Consequently, extensive research has been conducted to improve those properties while retaining their other desirable characteristics, primarily high and low temperature behavior. There have been a number of different approaches attempted to improve polysiloxanes. Among them, the most prominent include the

(1) metallosiloxanes: polysiloxanes in which some of the silicon atoms are replaced by metals (M = Al, Tn, Sn ...) as follows:



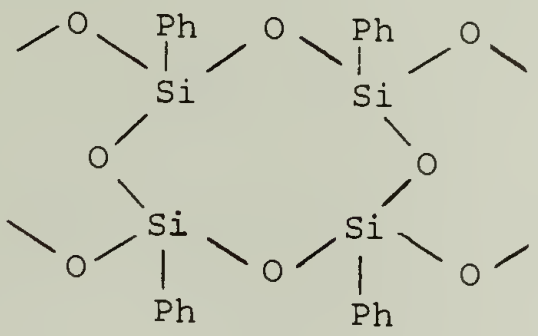
I

(2) polysilazenes: polymers having Si - N rather than Si - O linkages in their chains, as follows:



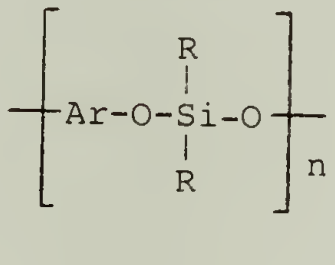
II

(3) <u>phenylsilsesquioxanes</u>: double-stranded siloxane chains framed with organic groups, as follows:



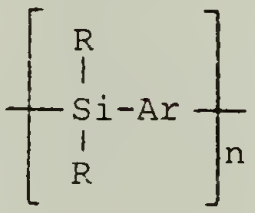
III

(4) <u>polyaryloxysilanes</u>: polymers in which every other silicon atom in the chain is replaced by an arylene group, as follows:



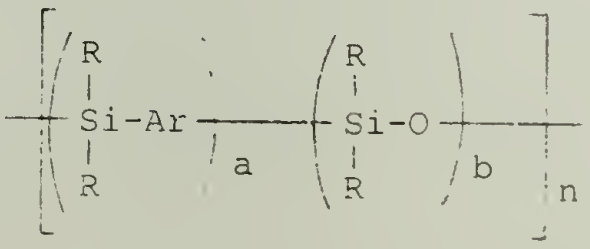
IV

(5) <u>polysilarylenes</u>: polymers in which all oxygen atoms in the basic siloxane structure are replaced by arylene groups, as follows:



V

(6) <u>poly(silarylenesiloxanes)</u>: polymers in which some of the oxygen atoms are replaced with arylene groups, as follows:

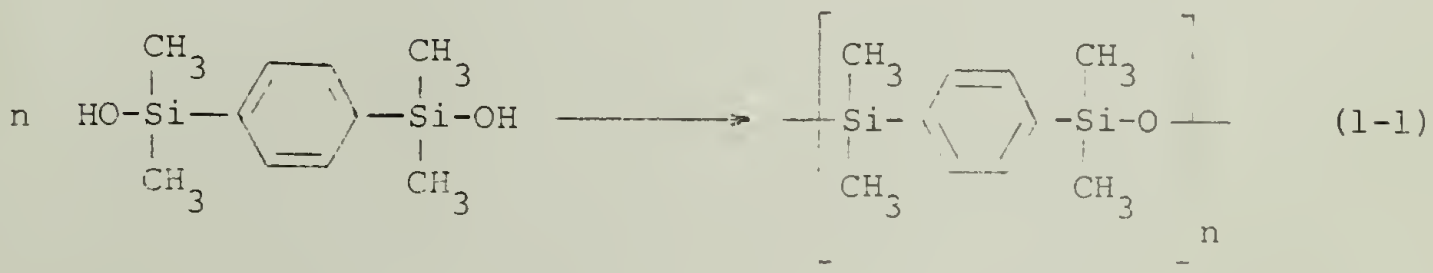


VI

In addition to these, a number of hybrid polymers which are combinations of silazene (Si-N), aryloxysilanes, carborane ($CB_{10}H_{10}C$) and siloxane structural units have been reported[13,27].

Among the modified siloxanes, those containing silarylene units have attracted significant attention, and considerable work has been done in this area[13]. These efforts were not fruitless, and they showed that a number of advantages result from the replacement of a portion of oxygen atoms in polysiloxanes by arylene groups. Such advantages include increased thermal stability, higher crystallinity[12], increased viscosity, improved mechanical properties, and others. The available data indicate that, of all the structures within this group, the exactly alternating silarylene-siloxane polymers might show the most desirable properties, of which high thermal stability with retained low temperature flexibility would probably be of prime importance[14]. This prediction is suggested from the data for silarylene-siloxane polymers, which have successions of two, three or more dimethyl-siloxane groups alternating with silarylene units, collected in Table 1-1[14].

Extensive research in this area started when, in 1951, Sweda prepared poly-p-phenylenetetramethyldisiloxane by the dehydration of 1,4-bis(dimethylhydroxysilyl)benzene, as shown in Reaction 1-1[15]:

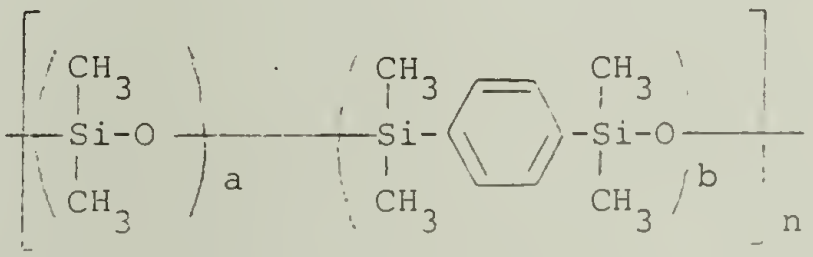


VII VIII (1-1)

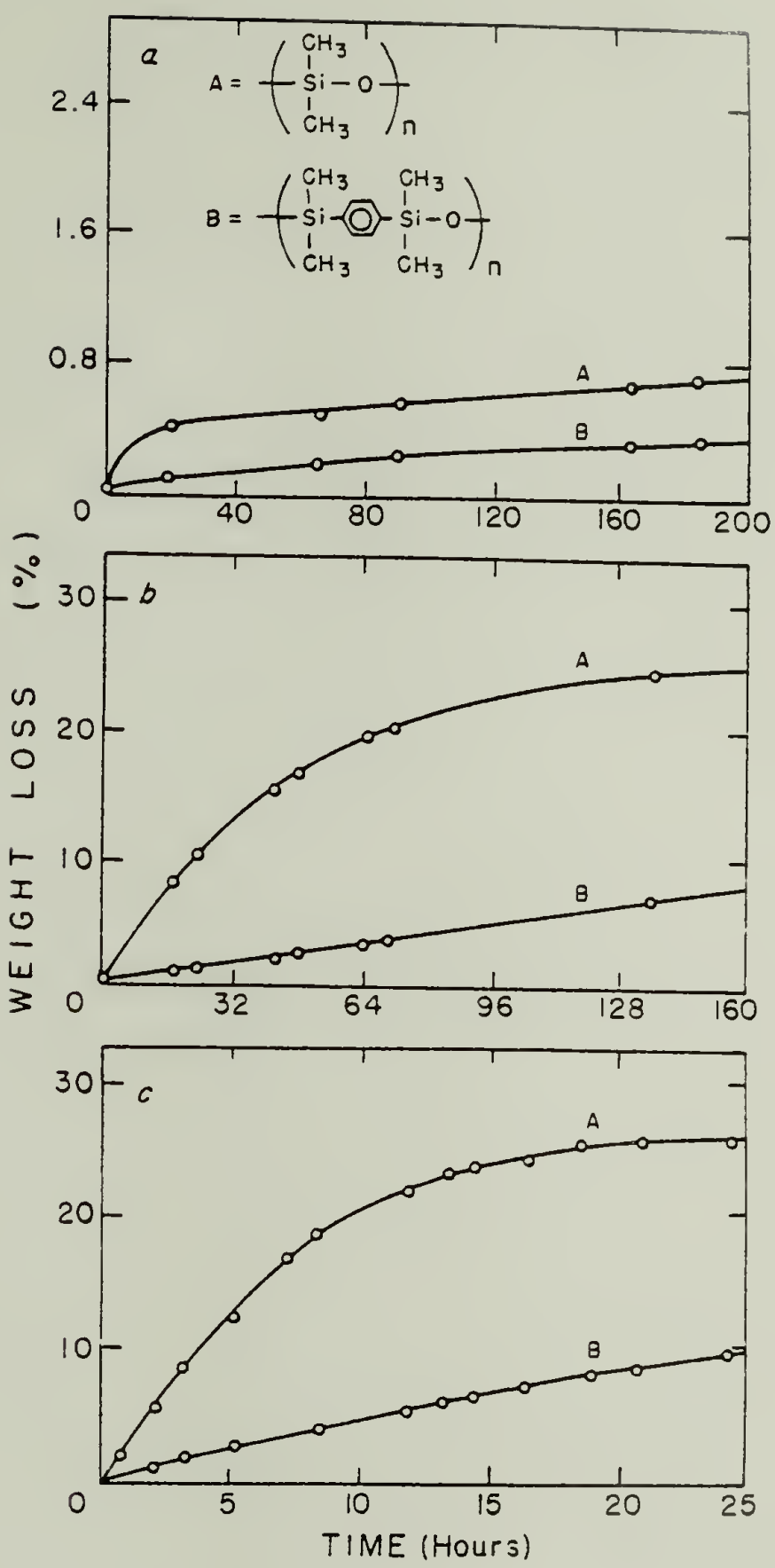
which is the closest to the alternating silarylene-siloxane structure. The properties of this polymer were carefully investigated and reported by Merker and Scott[16]. These authors realized that "no reproducible method for the preparation of truly high molecular weight polymers had been reported, nor are published methods of synthesizing possible monomers entirely satisfactory."

They reported preparation of 1,4-bis(dimethylhydroxysilyl) benzene from 1,4-bis(dimethylhydrogensilyl)benzene, which was obtained from p-dibromobenzene and dimethyldichlorosilane by use of an *in situ* Grignard technique. The polymer was obtained by condensation polymerization of the diol in benzene solution. It had in some cases weight-average molecular weights as high as 400,000 and was found to be more stable than poly(dimethylsiloxane) both to atmospheric oxidation and to volatile product formation in the temperature range 200-305°C, see Figures 1-1 to 1-3 for comparison of these two polymers. The authors also reported the crystalline melting point for poly-p-phenylenetetramethyldisiloxane to be 148°C and the heat of fusion $\Delta H_u = 4350$ cal/unit.

The same group of research workers prepared random and block copolymers of 1,4-bis(dimethylhydroxysilyl)benzene and α,ω-dihydroxypolydimethylsiloxanes[17] as follows:



IX



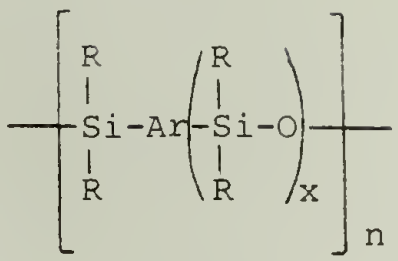
Figures 1-1 to 1-3 (a to c). Thermal stabilities of poly-p-phenylenetetra-methyldisiloxane and poly(dimethylsiloxane) in air at: 200°C (a); 255 C°(b) and 300°C (c).

These polymers were elastic at temperatures above their melting points, which ranged up to 148°C depending on the amount of the silphenylene component.

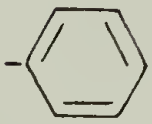
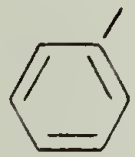
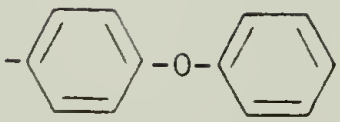
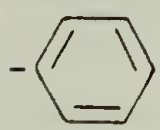
The authors could control the values of a and b in IX either by using hydroxy terminated poly(dimethylsiloxanes) of different degrees of polymerization or by preforming tetramethyl-p-silphenylene-siloxane units. It was concluded that, if the length of a segment was maintained at a constant value in the copolymers decreasing the ratio a/b resulted in higher tensile strengths and higher melting points with increased degree of crystallinity. However, the synthesis employed did not allow preparation of exactly alternating structures, which would be characterized by a = b = 1 and which would be expected to show the ultimate in those properties. Alternatively, if the ratio a/b was held constant, then increasing the length of a and b segments should lead to higher melting points and higher tensile strength reflecting an increase in the degree of crystallinity. These considerations also suggest that the exactly alternating incorporation of tough, crystalline fiber-forming[16] tetramethyl-p-silphenylene-siloxane units with elastomeric dimethylsiloxane units would greatly improve the mechanical and high temperature properties of the latter without greatly disturbing the very desirable elasticity and low temperature characteristics.

A more general method of preparation of poly-p-phenylene-dimethylsilyl-dimethylsiloxanes was that reported by Breed and co-workers in 1967[14]. They synthesized a series of polymers having

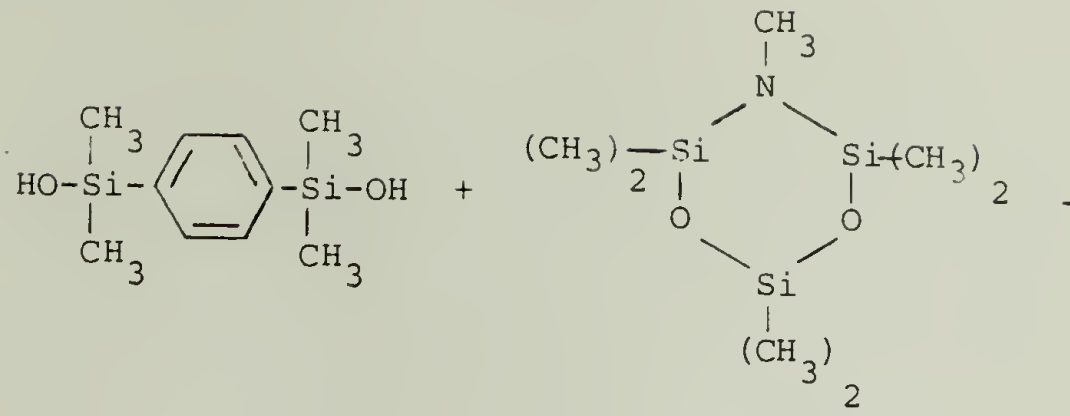
the following general formula:



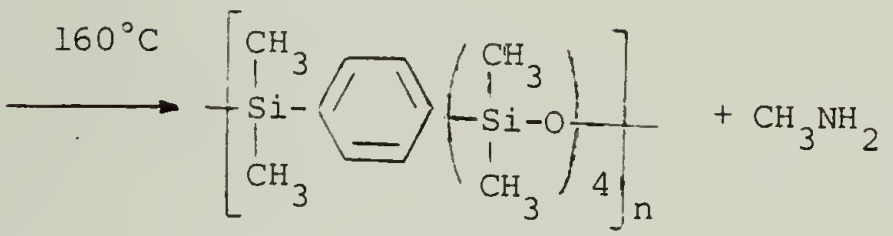
X

where: Ar =  ;  or  ; R = $-CH_3$ or  ; and x = 2; 3 and 4 (x = 1 is poly-p-phenylenetetramethyldisiloxane (VIII) already discussed [15,16]).

In 1961 Pike[18,19] reported a condensation reaction involving silylamines and silanols to form siloxanes under conditions in which there was no self-condensation of the silanol. Also, when applied to the condensation of arylenedisilanols with α,ω-bis(methylamino)-polysiloxanes, this method afforded a satisfactory route to the synthesis of arylene-modified siloxanes. Breed and coworkers modified this procedure[14] by employing N-methyl-siloxazenes for the polymerization rather than α,ω-bis(methylamino)polysiloxanes because the former were of greater hydrolytic stability and easier to prepare as follows:



(1-2)



XI

By combining different monomers they were able to prepare a series of different polymers as shown by the general structure X. They concluded that both the nature of the arylene group (Ar) present in the chain and the number of dimethylsiloxy groups (x) affected the thermal stability in such a manner that increasing the number of siloxy groups decreased the thermal stability of the polymers as shown in Figures 1-4 and 1-5. However, all of their polymers were significantly more stable than a typical commercial poly(dimethylsiloxane) gum which undergoes catastrophic decomposition under the same conditions at 300°C or below. This result showed that long segments of dimethylsiloxy groups can be present in the polymer before the degradation mechanism which is effective in poly(dimethylsiloxane) limits its thermal stability.

Another very significant result of this work was the observation that the changes in the length of the siloxane segments could be directly

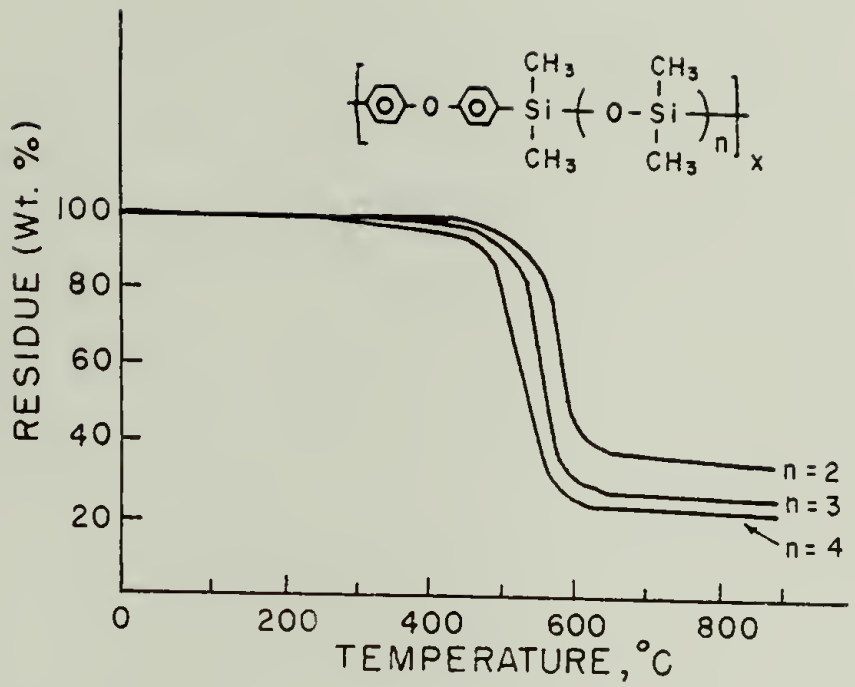


Figure 1-4. TGA in nitrogen for a series of silarylene-siloxane polymers containing diphenyl ether units.

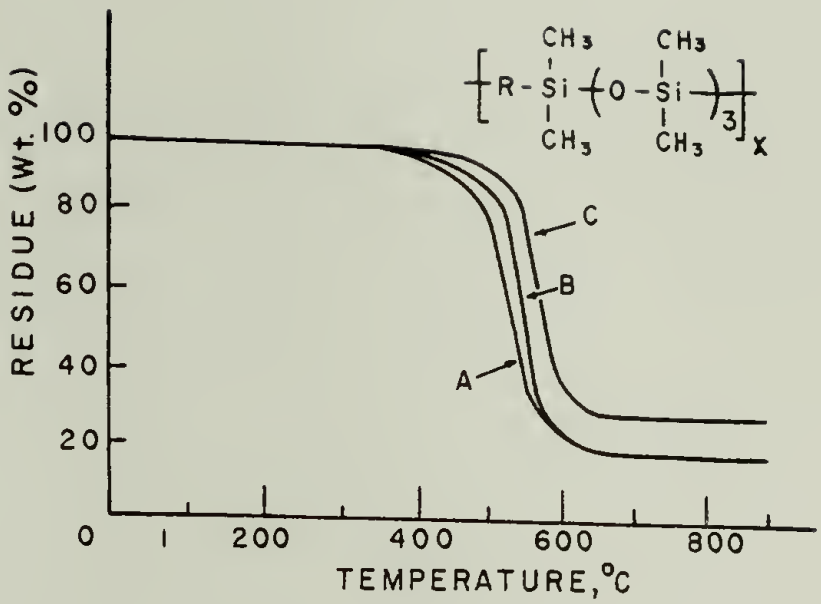


Figure 1-5. TGA in nitrogen for a series of silarylene-siloxane polymers containing the following arylene units: A: m-C_6H_4; B: p-C_6H_4; C: -C_6H_4-O-C_6H_4-.

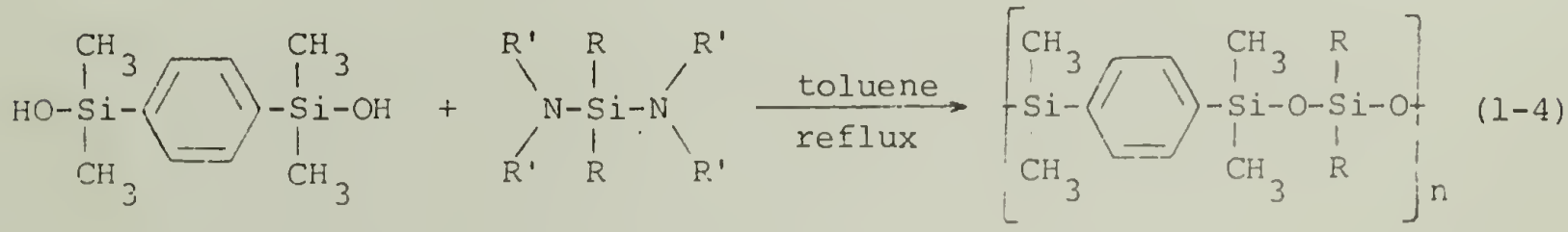
correlated with the changes in the glass transition temperature of the polymers (see Table 1-1). From the values in Table 1-1 by extrapolation to the number of dimethylsilyl groups in the segment equal to two, one can predict the values for the glass transition temperatures of the exactly alternating polymers as shown in Figure 1-6.

The weight-average molecular weights of the polymers were $8 \times 10^5 - 9 \times 10^5$ as determined by light scattering method and the following molecular weight-intrinsic viscosity relationship was obtained:

$$[\eta] = 1.12 \times 10^{-4} \times M_w^{0.75} \qquad (1\text{-}3)$$

Such a relationship had been earlier established by Merker and Scott in reasonably good agreement. The molecular weight dispersities about 3.5 probably resulting from the preparative techniques which were involved and which were to heat a mixture with slight excess of siloxazene over disilanol (to compensate for the loss of a more volatile monomer at 160°C) until a satisfactory high viscosity was reached.

In 1973, R.E. Burks reported the first work on strictly alternating silarylene-siloxane polymers[19], obtained by treating 1,4-bis-(dimethylhydroxysilyl)benzene with diaminosilanes:

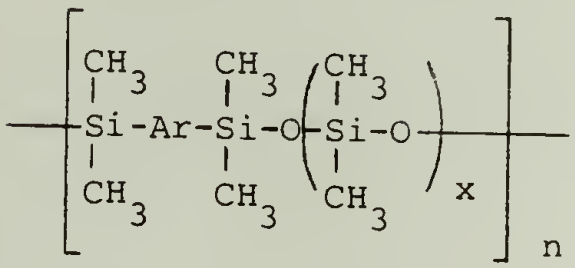


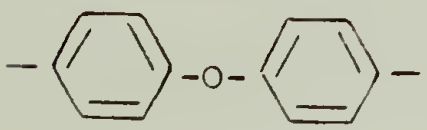
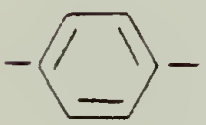
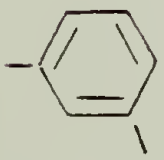
XII, XIII

+ 2 R'_2NH

TABLE 1-1

Glass Transition Temperatures and High Temperature Stability of Silarylene-Siloxane Polymers



Ar	x	Tg (°C)	TGA Temp. °C*
	2	-37	560
	3	-52	530
	4	-65	500
	2	-62	-
	3	-72	510
	4	-80	-
	3	-75	490

*Approximate temperature of initial knee in TGA curve at a heating rate of 15°C/min in N_2 atmosphere.

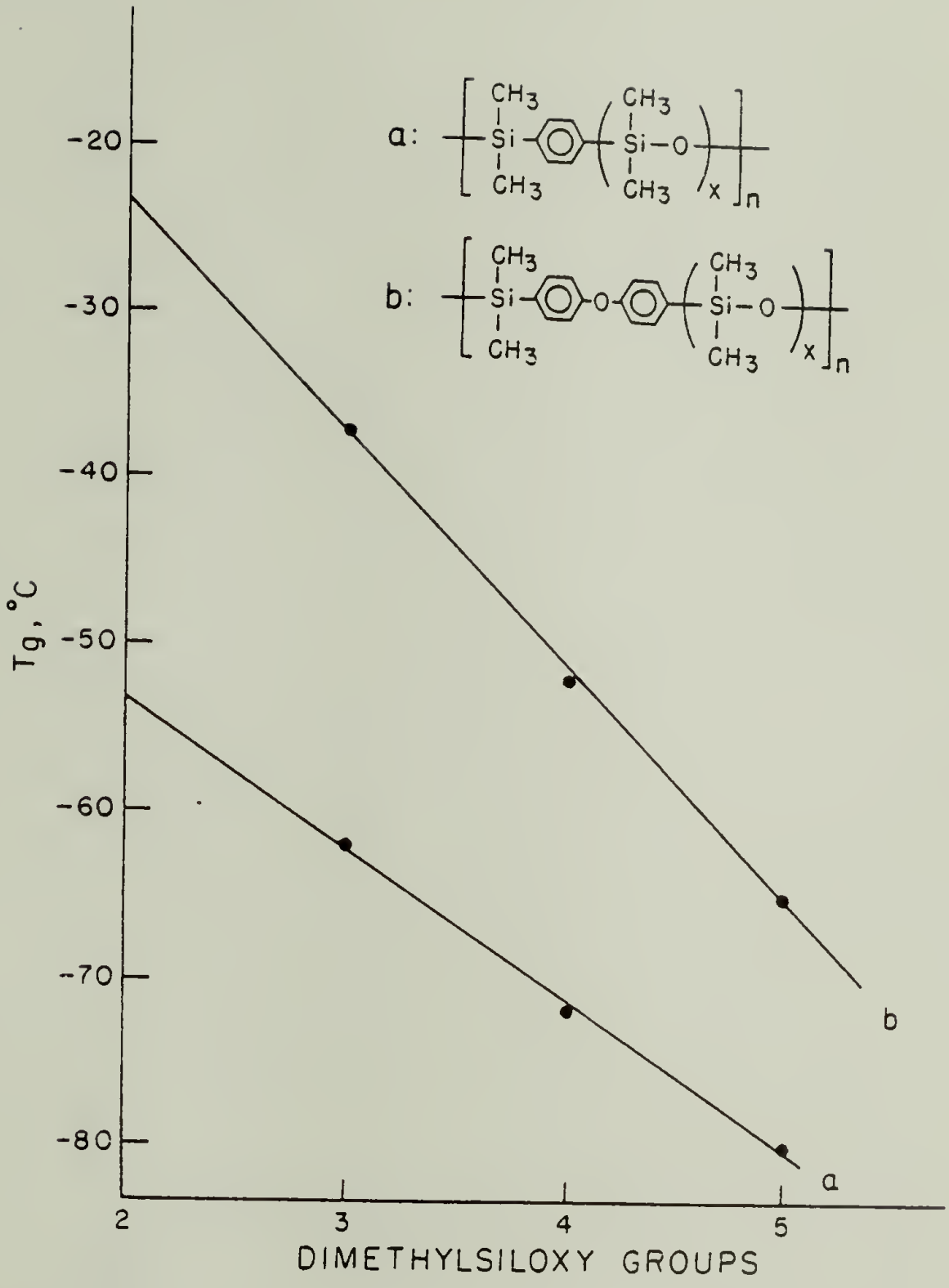


Figure 1-6. Dependence of glass transition temperature on the number of dimethylsiloxy groups in a segment for the polymers prepared by L.W. Breed et al. (Reference 14).

where: XII is for R = R´ = $-CH_3$, poly [1,4-bis(oxydimethylsilyl) benzene-dimethylsilane]; and XIII is for R= $-C_6H_5$ and R´ = $-CH_3$, poly [1,4-bis(oxydimethylsilyl)benzene-diphenylsilane].

This synthesis was another application of Pike's silylamine-silanol condensation reaction but this time with a silylamine monomer capable of producing an alternating polymer structure. In a typical experiment the polymerization reeaction (1-4) was started with slight excess of the disilanol (about 3 mole %) followed by additions of 0.5% of stoichiometric portions of the diaminosilane until the viscosity of the reaction mixture reached the desired level. In this manner the reaction was stopped when the molar ratio of the two monomers equalled 0.992; i.e., with 1.008% diaminosilane in excess. The polymer, which was precipitated from methanol, was obtained as a colorless, slightly cloudy viscous oil in 98% yield. It had an inherent viscosity of 0.98 dl/g at 30°C in tetrahydrofuran (1.0 g/dl).

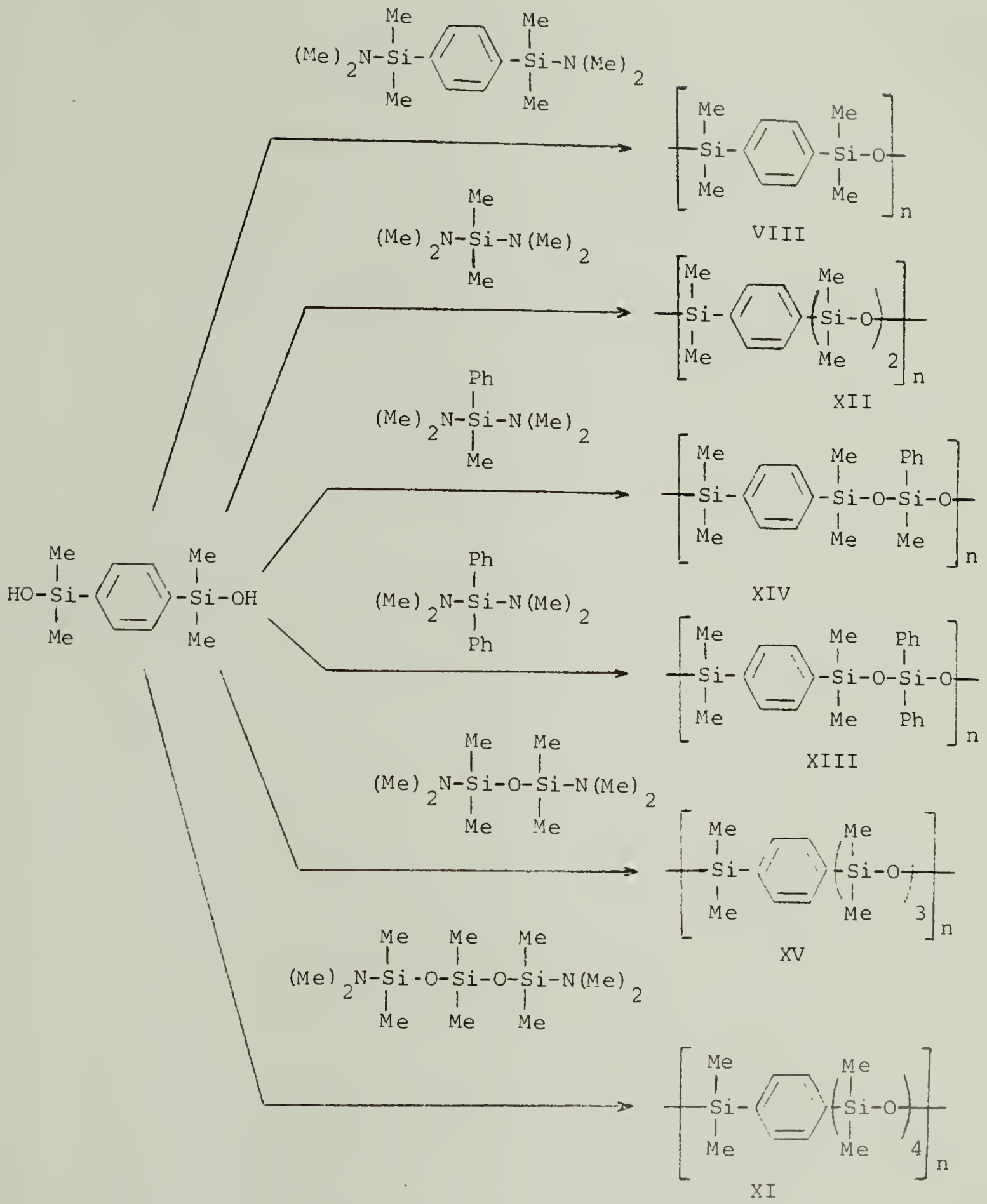
Poly [1,4-bis(oxydimethylsilyl)benzene-dimethylsilane], polymer XII above, obtained in such a way, had a glass transition at -63°C (by DSC) and it was readily cured to form an elastomer. The phenylene-substituted polymer, XIII, had a glass transition at 0°C , and it was slightly more thermally stable. For example, in a TGA experiment, it lost 10% of its weight at 460°C while the same loss was observed with polymer XII at 440°C.

Three years later in 1976, Pittman, Patterson and McManus described[20] the syntheses and characterization of a series of

silarylene-siloxane polymers. They employed 1,4-bis(dimethyl-hydroxysilyl)benzene, VII, in solution polycondensation reaction with different bis(dimethylaminosilanes) and described the monomer syntheses and polymerization reactions based upon their "aminosilane-deficient method." Some kinetic studies were also carried out[21-24].

In their work the polycondensation reactions were performed in toluene at 100°C. At the beginning, the reaction mixture had a slight molar deficiency (97% of theoretical) of the diaminosilane. After each hour of reaction time incremental additions (0.5% of the total stoichiometric quantity) of aminosilane were made. The progress of the reaction was monitored by inherent viscosity determination. It was observed in most cases that the viscosity reached a maximum at molar ratios of disilanol and aminosilane very close to unity. High polymers (molecular weights of the order of 10^5) were readily obtained. They ranged in appearance from viscous oils to stiff gums and were quite soluble in aromatic solvents and tetrahydrofuran. Synthetic work performed in these investigations could be summarized as shown in Reactions 1-5.

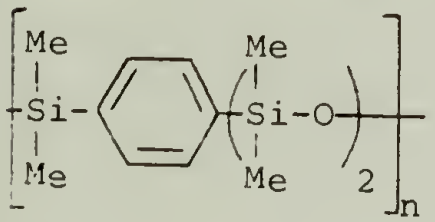
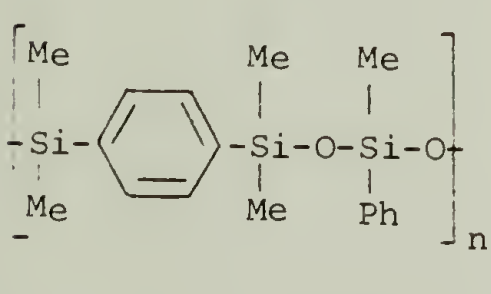
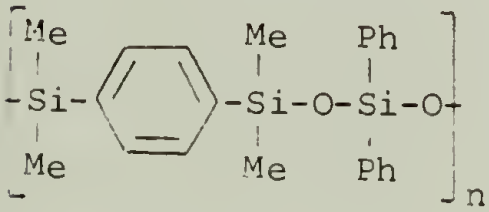
Detailed molecular weight studies were carried out using gel permeation chromatography and light scattering measurements in tetrahydrofuran at 30°C. Polymers were fractionated in order to evaluate the constants in Mark-Houwnik equation, which gave the results summarized in Table 1-2.


(Me)2N-Si(Me)2-C6H4-Si(Me)2-N(Me)2
VIII
(Me)2N-Si(Me)2-N(Me)2
XII
(Me)2N-Si(Me)(Ph)-N(Me)2
XIV
(Me)2N-Si(Me)(Ph)-N(Me)2
XIII
(Me)2N-Si(Me)2-O-Si(Me)2-N(Me)2
XV
(Me)2N-Si(Me)2-O-Si(Me)2-O-Si(Me)2-N(Me)2
XI
HO-Si(Me)2-C6H4-Si(Me)2-OH

Reaction (1-5)

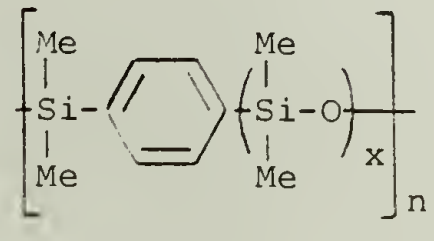
TABLE 1-2

Parameters for the Mark-Houwnik Equation for Silarylene-Siloxane Polymers in Tetrahydrofuran at 30°C

Polymer		$K \times 10^{-5}$	a
	XII	7.86	0.757
	XIV	5.34	0.799
	XIII	3.28	0.821

The increase in the coefficient a with increasing phenyl substitution in the polymer was attributed to a progressive increase in the hydrodynamic volume occupied by the random coil.

By use of torsional braid analysis (TBA) and differential scanning calorimetry (DSC) the glass transition temperatures were obtained and found to fall in a regular order for the following series of polymers:



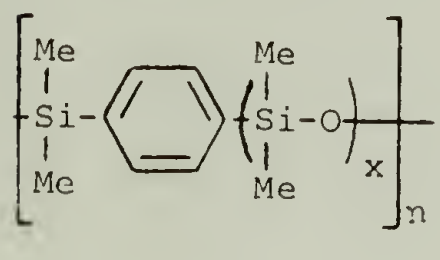
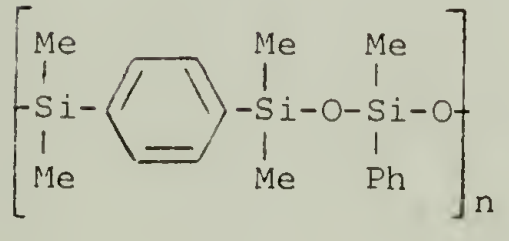
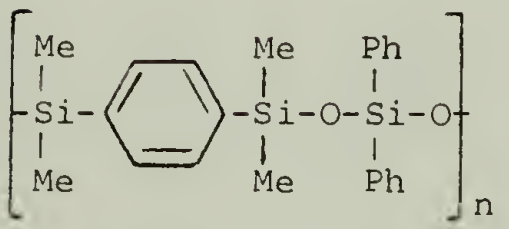
XVI

The polymers showed the dependence of glass transition temperature on x given in Table 1-3. These values are different from those previously reported for the same polymers[14]. The agreement between the TBA and DSC measurements led Pittman and coworkers[20] to suggest reconsideration of the glass transition temperatures reported by Breed[14]. Figure 1-7 and Table 1-4 compare the results of the two groups.

It is apparent from the data in Table 1-3 and Figure 1-7 that the contribution of dimethylsiloxy groups in decreasing the value of T_g is very large for the first few groups but quickly decays and very little additional decrease occurs beyond ten of these per repeating unit. If one compares the values from Table 1-3 with the glass transition temperatures of the following unmodified siloxanes:

TABLE 1-3

Glass Transition Temperatures for a Series of Silarylene-Siloxane Polymers

Polymer	Polymer	x	Tg, °C
	VIII	1	-25
	XII	2	-61
	XV	3	-88
	XI	4	-102
		5	-109
	XIV		-25
	XIII		+1

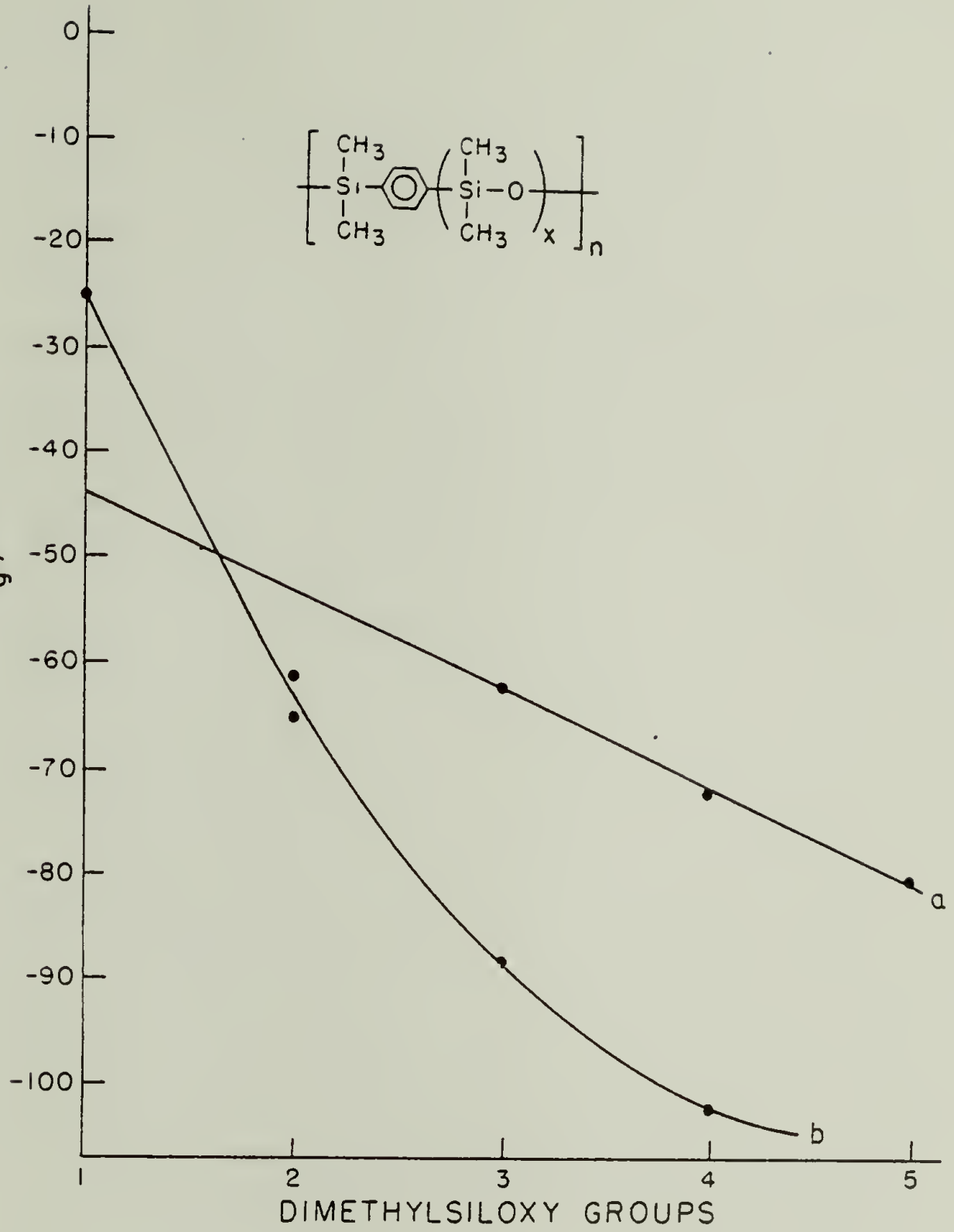
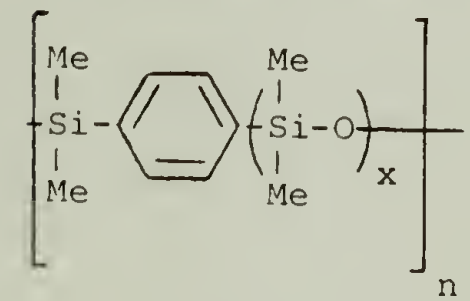


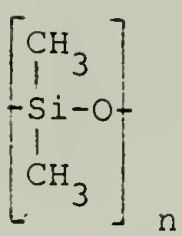
Figure 1-7. Comparison of the glass transition temperatures reported for silarylene-siloxane polymers, XVI, by: a: L.W. Breed et al. (Reference 14); b: C.U. Pittman, Jr. (Reference 20).

TABLE 1-4

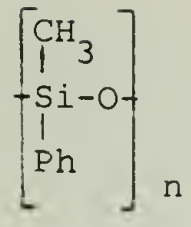
Differences in Values for Glass Transition Temperatures for the Series of Silarylene-Siloxane Polymers, XVI, as Reported by Breed[14] and Pittman[20]

Polymer	x	Tg, °C[14]	Tg, °C[20]	ΔTg, °C
	2	---	-61	8*
	3	-62	-88	26
	4	-72	-102	30
	5	-88	-109	21

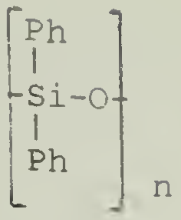
*A value for Tg, °C[14] was not reported in the reference but was obtained here from Figure 1-7.



XVII



XVIII



XIX

which were found to be -123°C[27]; -86°C[20] and -35°C[20], respectively, it follows that introduction of the aromatic units either into the main chain backbone or as a pendant group stiffens the chain and increases T_g.

TGA studies of the high temperature properties of silarylene-siloxane polymers in nitrogen by Pittman and-coworkers[20] gave the results shown in Figure 1-8.

These results show that the introduction of phenylene units into the main chain increased the overall thermal stability. Similarly, substitution of the methyl groups in dimethylsiloxy units by phenyl groups also increased the thermal stability. From Figure 1-8 it is seen that the temperature at which 10% loss was noticeable was 380, 410 and 445°C for polymers B, C and D, respectively. Compared to poly(dimethyl-siloxane), A, decreasing the value of x in the silarylene-siloxane polymers, XVI, increased the thermostability, and 10% weight loss was reported at 475, 380 and 355°C for polymers VIII, XII and poly(dimethyl-siloxane), respectively.

These results are perfectly consistent with present knowledge about the degradation of poly(dimethylsiloxane), XVII[26]. In an inert

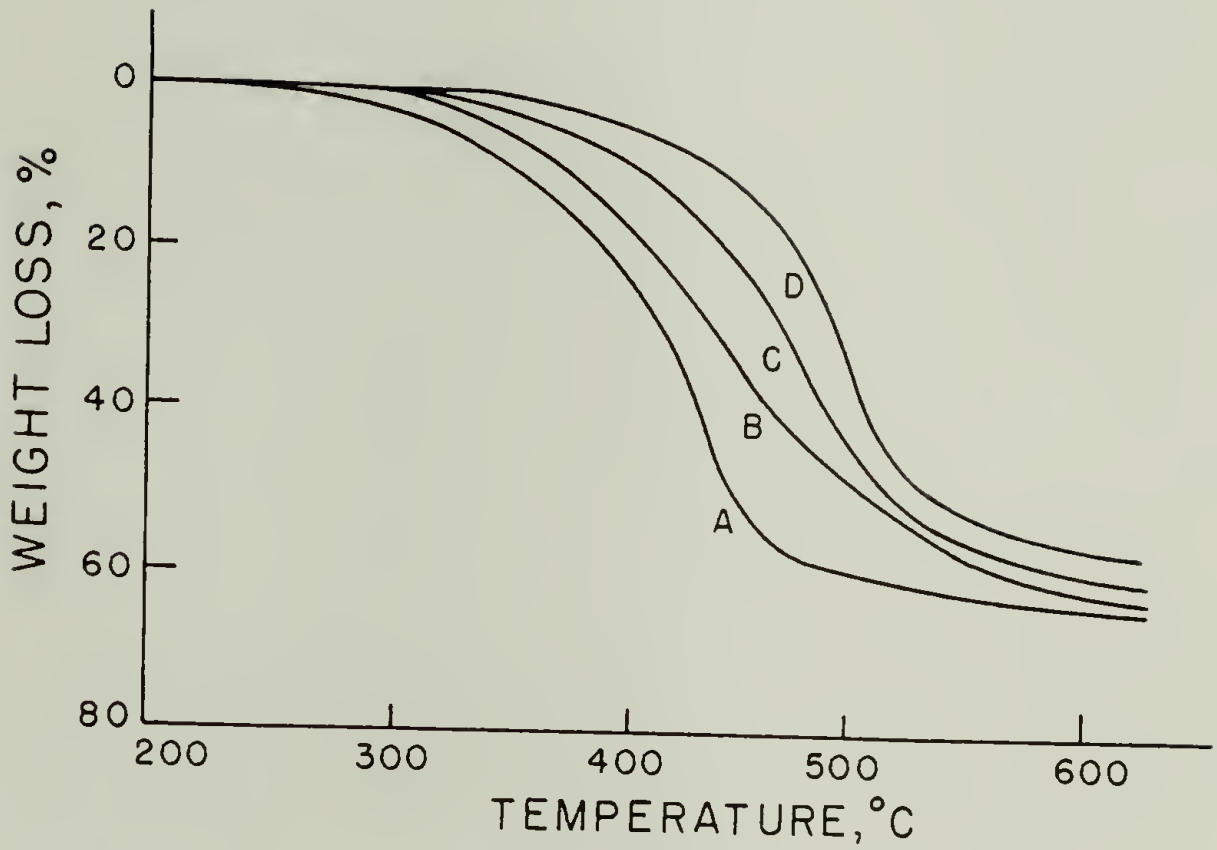
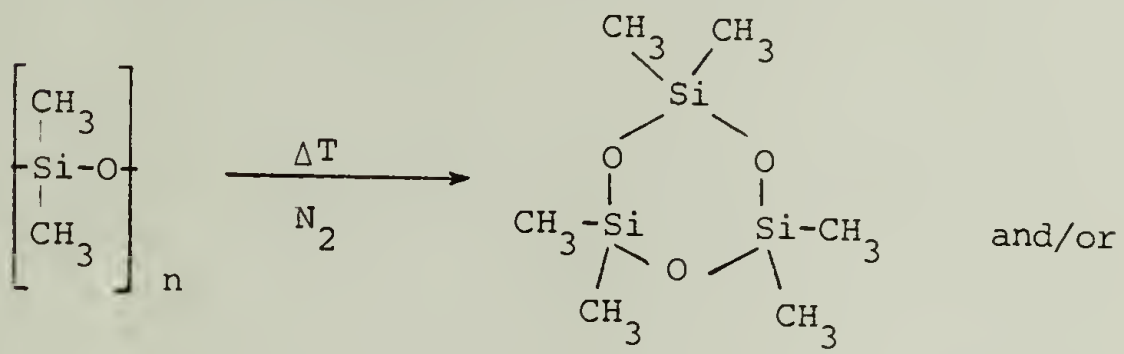
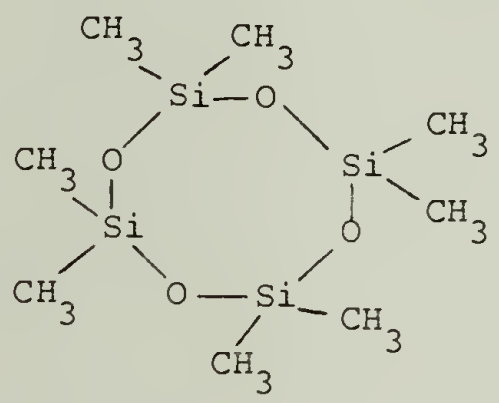


Figure 1-8. TGA thermograms in nitrogen for: A: poly(dimethylsiloxane); B: Polymer XII; C: Polymer XIV; D: Polymer XIII.

atmosphere, scission of the Si-O bond was followed by formation of cyclic structures such as six- or eight-membered siloxane rings which are thermodynamically extremely stable and easily form as follows:



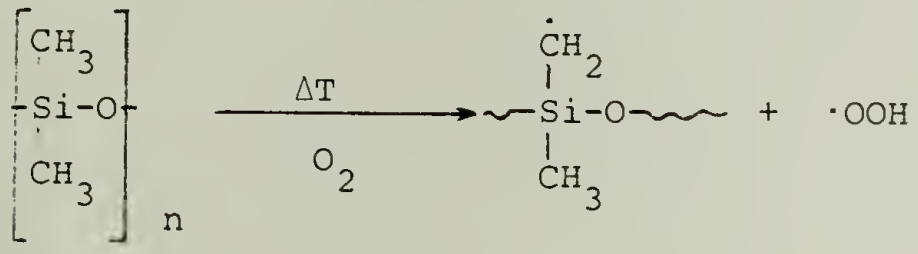
and/or



(1-6)

Introduction of stiff phenylene units into such a chain apparently retards or prevents the formation of cyclic structures compared to poly(dimethylsiloxane) and, in such a manner, these groups stabilize the entire polymer.

In air, on the other hand, the major degradation mode involves formation of the free radicals on the side chain groups, as follows:



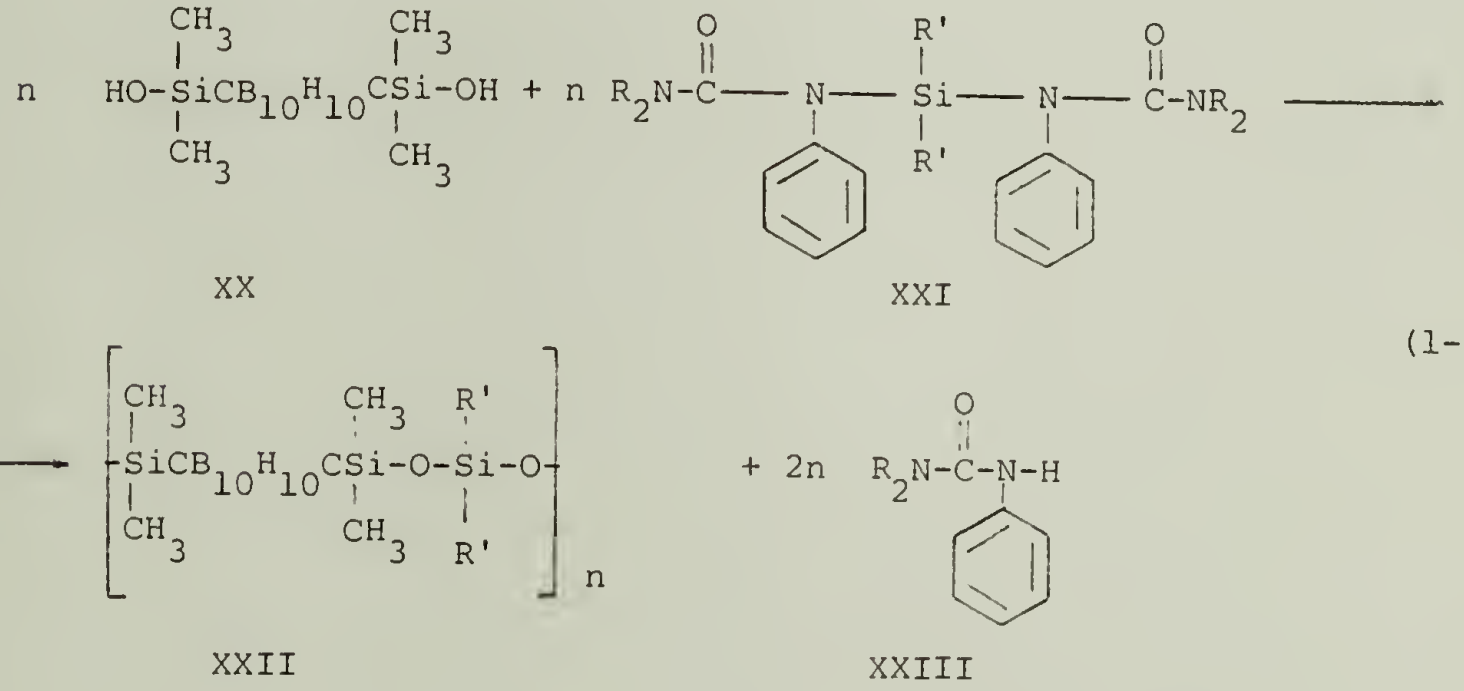
(1-7)

Substitution of pendant methyl groups by aromatic moieties prevents the formation of free radicals and stabilizes the polymer.

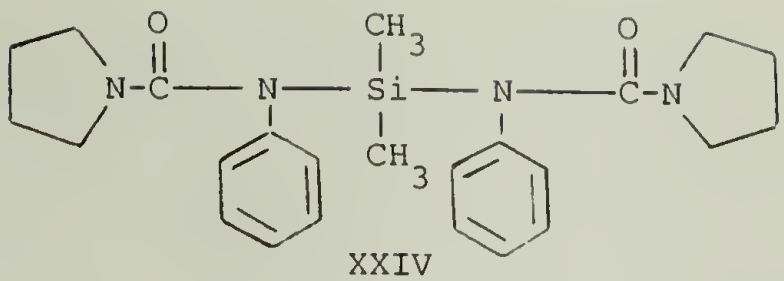
However, in spite of all these indications, from work carried out in the area of silarylene-siloxane polymers, that exactly alternating polymers of this structure would have very desirable properties there still has been no useful method developed for their preparation. The lack of the suitable synthesis was due to two reasons. Firstly, there was a lack of useful active difunctional silane monomer which would be capable of introducing silyl groups into a polymer chain through a condensation polymerization reaction with arylenedisilanols. Dialkylaminosilanes, used by Burks[19] and Pittman[20] apparently did not attract attention for this purpose. Secondly, aminosilanes and their related derivatives all have one major disadvantage: they release either acidic or basic leaving groups, while undergoing such a condensation polymerization reaction. This characteristic is the major obstacle to preparation of high molecular weight polymers because of the pronounced susceptibility of Ar-Si bonds to either acidic or basic attack. Obviously, if such is the case, the competition between chain-forming condensation reaction and chain-breaking Ar-Si scission results in products with lower molecular weights.

The solution to the problem of reactive by-product formation came in 1977 with the work of Hedaya and coworkers[25]. They developed a condensation polymerization reaction for the preparation of exactly alternating D_2-meta-carborane-siloxane polymers from carborane silanols and a new type of reactive silane monomers: (N,N-dialkyl-N'-phenylureido)silanes. This reaction, like any other step-growth

polymerization, is subject to the usual problems involved in obtaining high molecular weights; that is, to the necessity for nearly quantitative yields and conversions with very pure monomers under conditions of stoichiometric equivalence of the two monomers[28]. However, Hedaya and coworkers were able to overcome these problems both through the use of a reactive bisureidosilane monomer, XXI, which gave off a relatively neutral urea by-product, XXIII, as shown in Reaction 1-8, and by carefully monitoring the reaction by ^1H NMR spectroscopy to determine the most effective methods of combining the two monomers and of achieving stoichiometric equivalence.



Of the bis-ureidosilanes investigated, the best monomer for the purpose was found to be the pyrrolidinyl compound, or bis(1,1-tetramethylene-3-phenylureido)dimethylsilane, XXIV:



XXIV

Lower polymerization temperatures were found necessary to prevent the self-condensation of the carborane silanols which would unbalance the functional group equivalence and prevent the achievement of high molecular weights. Monomer purity was also found to be particularly important, as was the method and order of addition of the two monomers in the reaction. When all of these precautions were taken, including use of the most reactive monomer with the least reactive by-products, and the proper conditions were applied, polymers with molecular weights well over 100,000 were obtained[25].

These polymers, however, had some disadvantages, which were principally their high cost, the high molecular weight of the carborane unit and their relatively high glass transition temperature (-42°C) and degree of crystallinity. The melting point of these polymers was approximately 92°C. On the other hand, the excellent thermal stability and mechanical strength of the exactly alternating carborane-siloxane polymers showed that such an alternating structure of rigid units and flexible siloxane units is a very desirable combination, as was already predicted from the known silarylene-siloxanes for the

achievement of good high temperature performance without excessive loss of low temperature flexibility.

The original idea for the work that will be detailed in the following chapters was based upon these considerations and on the drawbacks of the carborane-based polysiloxanes[13]. It was felt that preparation of exactly alternating silarylene-siloxane polymers should be reinvestigated using the breakthroughs of the work of Hedaya and coworkers in an attempt to prepare polymers with high molecular weight under mild and readily-controllable reaction conditions. Previous work on these polymers had clearly demonstrated that silarylene-siloxane polymers were capable of having outstanding thermal stabilities combined with low glass transition temperatures[19,20]. While exactly alternating polymers of this type had not been reported to any larger extent, previous conclusions could have been drawn from the properties of closely related polymers containing a succession of two or three dimethylsiloxane groups[14]. From the data available (Table 1-1) it was possible to estimate the properties like glass transition temperature (about -60°C for the polymers from 1,4-bis(dimethylhydroxysilyl)benzene) or thermal stability (above 400°C for the same polymers) and it was felt that such materials would be technologically and scientifically important.

Based upon these considerations investigations were initiated to prepare exactly alternating polymers through the reaction of different arylenedisilanols and bisureidosilanes, and to study their physical properties, particularly at extreme temperatures.

Bibliography

1. C. Friedel, J.M. Crafts, "Ueber einige neue organische Verbindungen des Siliciums and das Atomgewicht dieses Elements", Ann. Chem. Justus Liebigs, 127, 28 (1863).
2. A.D. Goddard, D. Goddard, "Textbook of Inorganic Chemistry", Vol. XI, Pt. I, Lippincott, Philadelphia, Pennsylvania (1928), p. 246.
3. F.S. Kipping, "Organic Derivatives of Silicon. Preparation of Alkylsilicon Chlorides", Proc. Chem. Soc., 20, 15 (1904).
4. F.S. Kipping, "Organic Derivatives of Silicon", Proc. Chem. Soc., 21, 65 (1905).
5. F.S. Kipping, "Organic Derivatives of Silicon. Part XVI. The Preparation and Properties of Diphenylsilicanediol", J. Chem. Soc., 101, 2108 (1912).
6. F.S. Kipping, L.L. Loyd, "Organic Derivatives of Silicon. Triphenylsilicol and Alkyloxysilicon Chlorides", J. Chem. Soc., 79, 449 (1901).
7. F.S. Kipping, J.E. Stands, "Organic Derivatives of Silicon. Part XXV. Saturated and Unsaturated Silicohydrocarbons Si_4 Ph_8", J. Chem. Soc., 119, 830 (1921).
8. J.F. Hyde, R.C. DeLong, "Condensation Products of the Organosilane Diols", J. Am. Chem. Soc., 63, 1194 (1941).
9. R.R. McGregor, E.L. Warrick, "Dialkylated Silicon Esters and Method of Making Them", U.S. Patent 2,380,057 (July 10, 1945).

10. E.G. Rochow, "The Direct Synthesis of Organosilicon Compounds", J. Am. Chem. Soc., 67, 963 (1945); "Preparation of Organosilicon Halides", U.S. Patent 2,380,995 (Aug. 7, 1945).

11. K.A. Andrianov, "Metalorganic Polymers", Volume 2, Interscience, New York (1967).

12. F.P. Price, "The Structure of High Polymer Spherulites", J. Polymer Sci., 37, 71 (1959).

13. W.R. Dunnavant, "Silarylene and Silarylene-Siloxane Polymers", Inor. Macromol. Rev., 1, 165 (1971).

14. L.W. Breed, R.L. Elliot, M.E. Whitehead, "Arylene-Modified Siloxanes", J. Polymer Sci., A-1, 5, 2745 (1967).

15. M. Sveda, "Polyarylene-Siloxanes and Processes for Making Same", U.S. Patent 2,562,000 (July 24, 1951).

16. R.L. Merker, M.J. Scott, "Preparation and Properties of Poly (tetramethyl-p-Silphenylene-Siloxane)", J. Polymer Sci., part A, 2, 15 (1964).

17. R.L. Merker, M.J. Scott, G.G. Haberland, "Random and Block Co-polymers of Poly(tetramethyl-p-Silphenylene-Siloxane) and Poly(dimethylsiloxane)", J. Polymer Sci., part A, 2, 34 (1964).

18. R.M. Pike, "Chemistry of the Silylamines. II. The Condensation of Silylamines with Silanediols", J. Polymer Sci., 50, 151 (1961).

18a. R.M. Pike, "Chemistry of the Silylamines. I. The Condensation of Monofunctional Silylamines with Monofunctional Silanols", J. Org. Chem., 26, 232 (1961).

19. R.E. Burks, Jr., E.R. Covington, M.V. Jackson, J.E. Curry, "Copolymers and Elastomers with Alternating Dioxysilphenylene and Silane Units", J. Polymer Sci., Polymer Chem. Ed., 11, 319 (1973).

20. C.U. Pittman, Jr., W.J. Patterson, S.P. McManus, "Oxysilane Polymers from Silanediol-Bis(dimethylamino)silane Polycondensations: Synthesis and Properties", J. Polymer Sci., Polymer Chem. Ed., 14, 1715 (1976).

21. C.U. Pittman, Jr., W.J. Patterson, S.P. McManus, "Organometallic Polymers. XV. Synthesis and Characterization of Some Ferrocene-Containing Oxysilane Polymers from Bis(dimethylamino) silanes", J. Polymer Sci., A-1, 9, 3187 (1971).

22. W.J. Patterson, D.E. Morris, "Polymerizable Siloxane Precursors Having In-Chain Perfluoroalkyl Groups", J. Polymer Sci., A-1, 10, 169 (1972).

23. W. J. Patterson, S.P. McManus, C.U. Pittman, Jr., "Organometallic Polymers. XXIX. Synthesis and Characterization of Ferrocene-Containing Soloxane Polymers from Bis(dimethylamino)silane-Disilanol Condensation", J. Polymer Sci., Polymer Chem. Ed., 12, 837 (1974).

24. S.P. McManus, W.J. Patterson, C.U. Pittman, Jr., "Polymerization and Reaction Rate Studies on Substituted Phenylmethylbis (dimethylamino)silanes", J. Polymer Sci., Polymer Chem. Ed., 12, 825 (1974).

25. E. Hedaya, T.H. Kawakami, P.W. Kopf, G.T. Kwiatkowski, D.W. McNeil, D.A. Owen, E.N. Peters, R.W. Tulis, "D_2-meta-Carborane-Siloxanes. IV. Syntheses of Linear, High Molecular Weight Polymers", J. Polymer Sci., Polymer Chem. Ed., 15, 2229 (1977).

26. K.A. Andrianov, "Metalorganic Polymers", Volume I, Interscience, New York (1965).

27. H.K. Lictemalner, M.N. Sprung, "Silicones", Encyclopedia of Polymer Science, Vol. 12, 465 (1970).

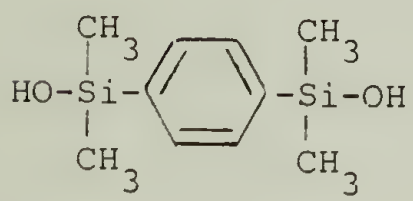
28. R.W. Lenz, "Organic Chemistry of Synthetic High Polymers", Interscience, New York (1967), p. 53 ff.

C H A P T E R I I

PREPARATION AND CHARACTERIZATION OF ARYLENEDISILANOLS

A. Introduction

The monomers selected for investigation during the initial period of this work were the following four different arylenedisilanols:



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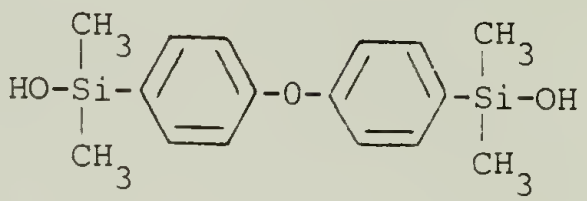

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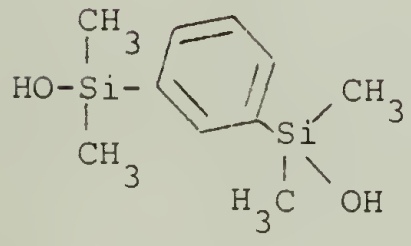
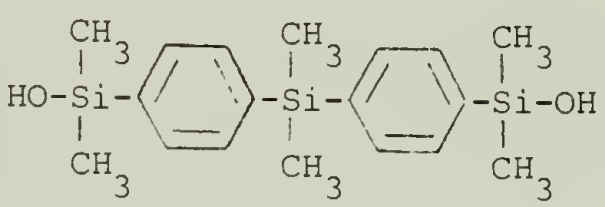


III



IV

Of these, results indicated that the most promising candidates were 1,4-bis(dimethylhydroxysilyl)benzene (I) and 4,4'-bis(dimethylhydroxysilyl)phenyl ether (II), and consequently detailed polymerization studies were concentrated later on these two. The selection was made on the basis of ease of preparation and purification, reactivity in polymerization with bis(1,1-tetramethylene-3-phenylureido)dimethylsilane,

ability to prepare high molecular weight polymers and polymer properties.

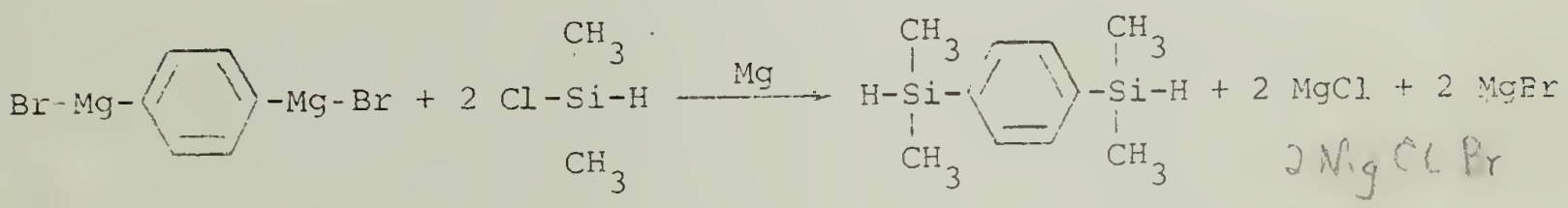
Although procedures for preparation of these arylenedisilanols had been developed by other workers some modifications were introduced during the course of this work. The improvements achieved by those modifications were in easier preparative procedures, increased yields and higher purities of the products.

This chapter describes in detail the syntheses and characteristics of both 1,4-bis(dimethylhydroxysilyl)benzene (I), termed p-diol and 4,4'-bis(dimethylhydroxysilyl)phenyl ether (II), termed ether-diol.

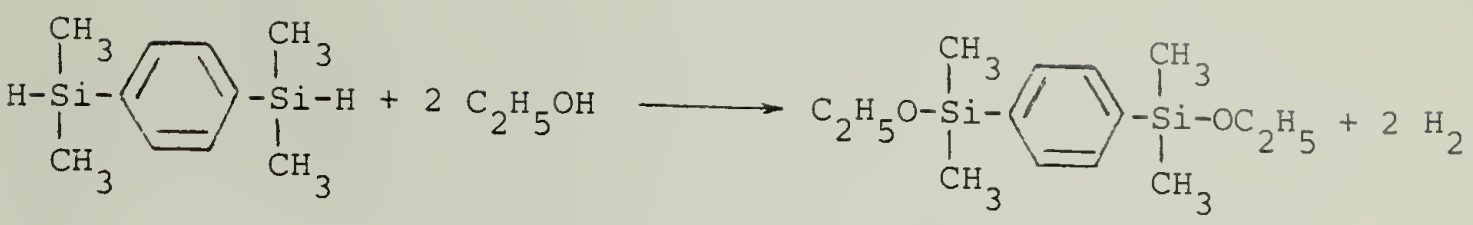
B. Preparation of 1,4-bis(dimethylhydroxysilyl)benzene (I)

This arylenedisilanol is obtained by hydrolysis of corresponding diethoxy derivative (VI), which is prepared by reaction of the Grignard reagent from p-dibromobenzene with dimethylchlorosilane to form 1,4-bis(dimethylhydrogensilyl)benzene (V), as follows:

(2-1)



V



VI

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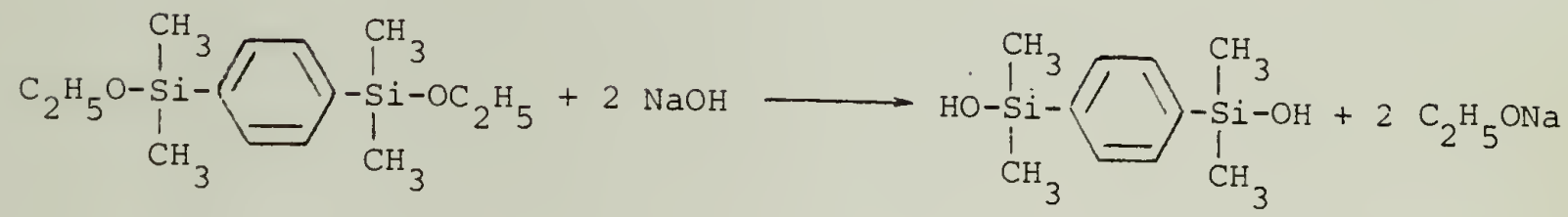


I

C. Experimental

1. Preparation of 1,4-bis(dimethylhydrogensilyl)benzene (V)

This compound was prepared by modification of the procedure described by Sorenson and Campbell[1], which had originally been reported by R.L. Merker and M.J. Scott[2].

Diethyl ether was refluxed for 12 hours over sodium lamelae (approximately 5 mm in diameter) and slowly distilled. This procedure was repeated once more before the solvent was finally refluxed and distilled from sodium and potassium. Magnesium turnings and Eastman

p-dibromobenzene were used without further purification. Dimethyl-chlorosilane obtained from Aldrich was distilled before use (B.P. 35°C).

A three-necked, one liter, round-bottomed flask was equipped with a mechanical stirrer, dry-ice condenser and a dropping funnel. The entire apparatus was assembled hot from the oven, thoroughly flamed under vacuum and flashed several times with prepurified nitrogen, which was first passed through a system of columns containing H_2SO_4, KOH pellets, P_2O_5 and molecular sieves ("Linde" type 3A, 1/16"). After the inert atmosphere was established, 36.5g (1.5g-atom) of magnesium turnings was placed into the flask and heated under nitrogen for about eight hours. The apparatus was then allowed to slowly cool down to room temperature and 500 ml of dry diethyl ether were charged. Under strong nitrogen purge the empty dropping funnel was removed and 177g (0.75 m) of p-dibromobenzene was added. Stirring was started and enough time was allowed for the dibromobenzene to dissolve. When solution was completed another dropping funnel containing 212.5g (2.25 m) of dimethylchlorosilane was attached to the flask under the strong nitrogen purge. The rate of addition of this silane compound was governed by the refluxing of the solvent from the heat of reaction. The reaction products were refluxed for one hour after addition was complete, poured over crushed ice, washed with water and finally dried over sodium sulfate. The mixture was stripped of the solvent and 109g (74.91% yield) of 1,4-bis(dimethylhydrogensilyl) benzene (V) was isolated by vacuum distillation; (B.P. 60-61°C/1.5 mm).

2. Preparation of 1,4-bis(dimethylhydroxysilyl)benzene (I)

The most convenient method for preparation of p-diol (I) is that described by Sorenson and Campbell[1].

A three-necked, one liter, round-bottomed flask was equipped with a mechanical stirrer, dry-ice condenser and a dropping funnel. The apparatus was assembled while all the parts were still hot from the oven and dried as in the preparation of compound (V). After the inert atmosphere was established, 120 ml of absolute ethanol were added from syringe and brought to a slow reflux. To this 95g (0.49 m) of previously prepared 1,4-bis(dimethylhydrogensilyl)benzene were added dropwise. After evolution of hydrogen had ceased, the reaction products were poured with constant stirring into a mixture of 57g NaOH, 350 ml CH_3OH and 40 ml H_2O. To this was added a solution of 57g NaOH in 380 ml H_2O. After standing for about 30 min, this mixture was poured with constant stirring into a solution of 505g KH_2PO_4 in excess ice and water. The precipitate which immediately formed was filtered and thoroughly washed with water until neutral to litmus paper. The crude product was recrystallized from benzene giving a final yield of 93g (85%) of 1,4-bis(dimethylhydroxysilyl)benzene or p-diol (I).

Purity of p-diol, prepared in the manner described above, was determined by elemental analysis, ^1H NMR spectroscopy and melting point. After recrystallization the compound showed a sharp melting point at 136-137°C. The ^1H NMR spectrum in deuterated dimethyl sulfoxide contained the following peaks: $Si-CH_3$ (singlet) at δ = 0.25 ppm; -OH (singlet) at δ = 5.88 ppm; $-C_6H_4-$ (singlet) at

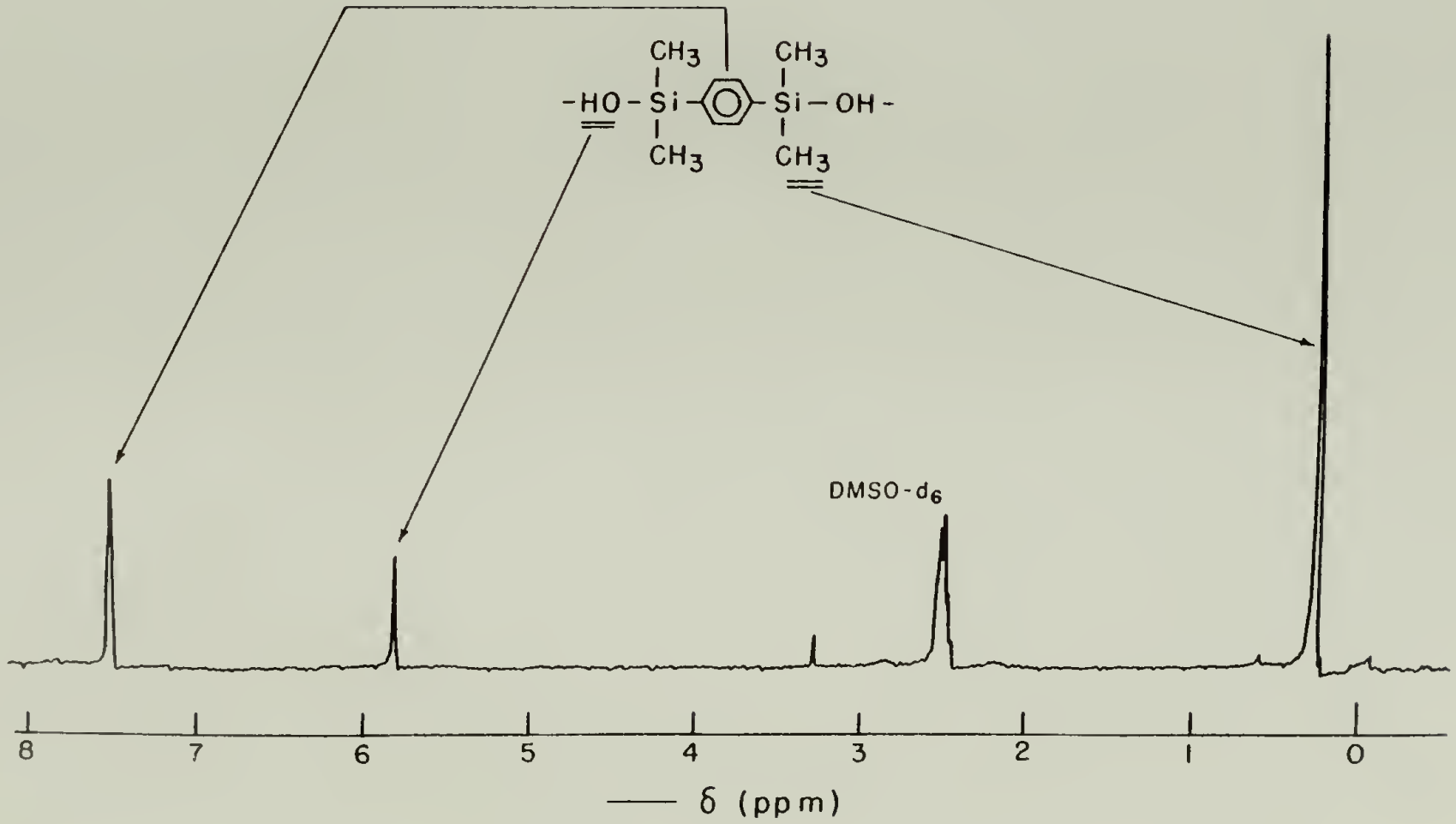


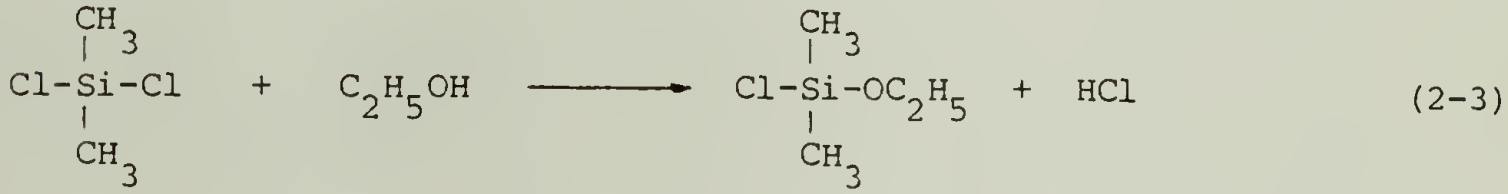
Figure 2-1. ^{1}H NMR spectrum of 1,4-bis(dimethylhydroxysilyl)benzene (p-diol) in deuterated dimethyl sulfoxide at 90 MHz.

δ = 7.48 ppm, and it is shown in Fugure 2-1.

Anal. calcd. for $C_{10}H_{18}O_2Si_2$: C, 53.10%; H, 7.96%; Si, 24.78%. Found: C, 51.99%; H, 8.24%; Si, 25.36%.

D. Preparation of 4,4'-bis(dimethylhydroxysilyl)phenyl ether (II)

4,4'-bis(dimethylhydroxysilyl)phenyl ether (II), termed ether-diol, is obtained by hydrolysis of corresponding diethoxy compound (VIII), which is prepared by the Wurtz reaction of dibromodiphenyl ether and dimethylethoxychlorosilane (VII) as follows:



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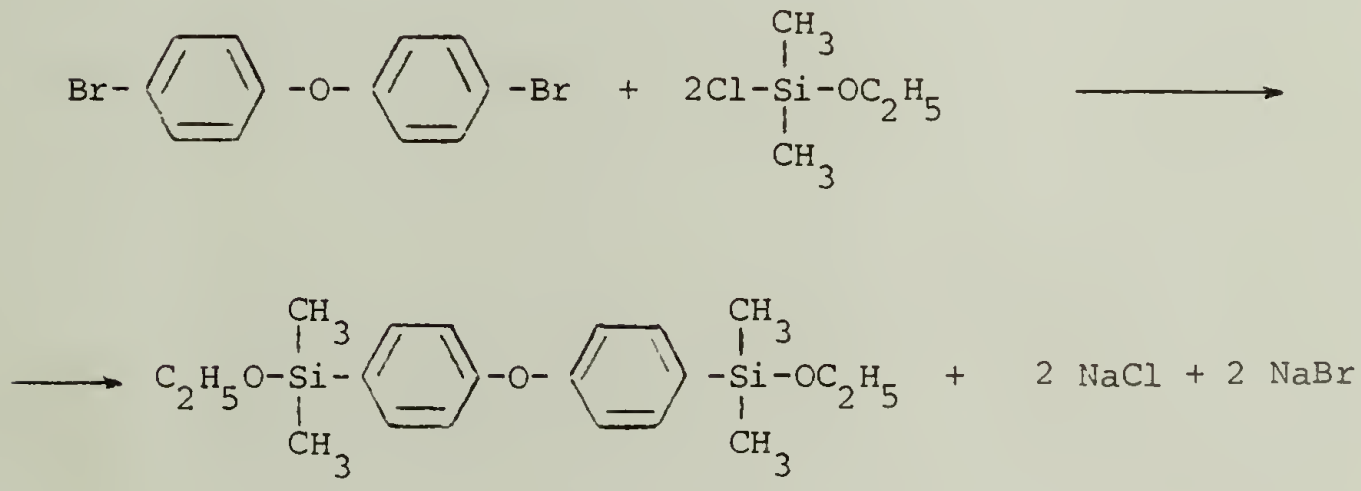
VII



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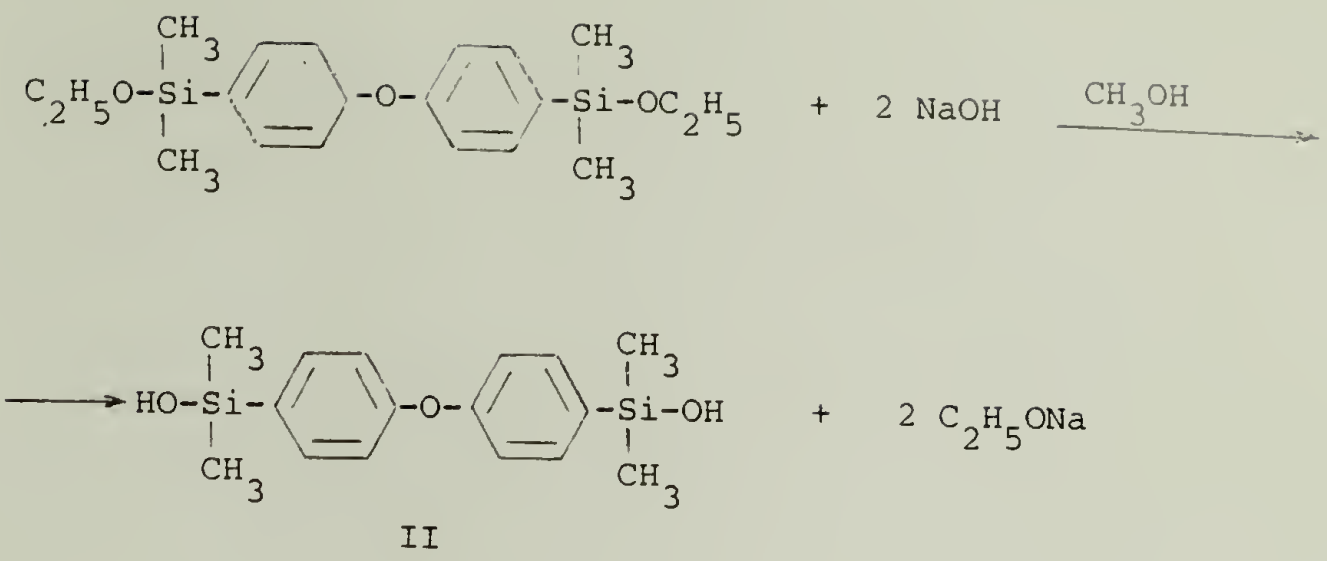
VIII



(2-5)

II

E. Experimental

1. Preparation of Dimethylethoxychlorosilane (VII)

This intermediate was prepared according to the procedure originally described by Bilow, Lawrence and Patterson[3].

Ethanol was refluxed and distilled twice over sodium metal, followed by another reflux and distillation over magnesium turnings activated by iodine[4]. The fraction which boiled at 78°±0.1 C was collected under an inert atmosphere. Dimethyldichlorosilane from Aldrich Chem. Co. was purified by distillation prior to use (B.P. 70°C).

Anhydrous ethanol (55.2g 1.2 m) was added dropwise to dimethyldichlorosilane (206g, 1.6 m). When the evolution of HCl gas subsided, the mixture was heated at reflux for another hour and distilled. The fractions separated are given in Table 2-1.

TABLE 2-1

Fractionation of the Products from Preparation of Dimethylethoxychlorosilane

Fraction	Boiling Temperature, °C	Weight, g
1	63-81	-
2	81-87	-
3	88-90	18.54
4	90-93	10.46
5	93-95	107.22
6	95	110.08
7	>95	8.40

A Varian Gas Chromatograph, Model 3700, was used to examine the nature of the collected fractions. The analysis conditions were as follows: column: 3.0% OV 101 on Chromosorb W-HP, column temperature: 70°C and constant, injector temperature: 120°C, carrier gas: He, flow rate: 30 ml/min and detector temperature: 200°C.

The chromatograms obtained from this analysis are shown in Figure 2-2. The results indicate that the reaction mixture consisted of three main components: A, B and C. Compound A showed the same retention time as pure dimethyldichlorosilane. Product B corresponded to dimethylethoxychlorosilane and it was isolated as the main cut at 95°C. Compound C, the high boiling fraction, was most probably dimethyldiethoxysilane. It is noticeable in Figure 2-2 that even the purest of the fractions still contained some small amounts of compounds A and B (fraction 6 in Figure 2-2). Thus, in order to obtain the pure product it had to be redistilled. Relative compositions of the fractions from Figure 2-2 are shown in Table 2-2.

To isolate pure dimethylethoxychlorosilane, Fractions 5 and 6 from this distillation were combined together and fractionation was repeated. The main cut was collected at 95°C. A total of 117.2g (53% yield) was obtained, and a single peak in the GC analysis confirmed the purity. The original reference[3] reported a 17% lower yield. The difference in yield may have been due to the slower addition of ethanol and longer reaction time allowed in the present preparation.

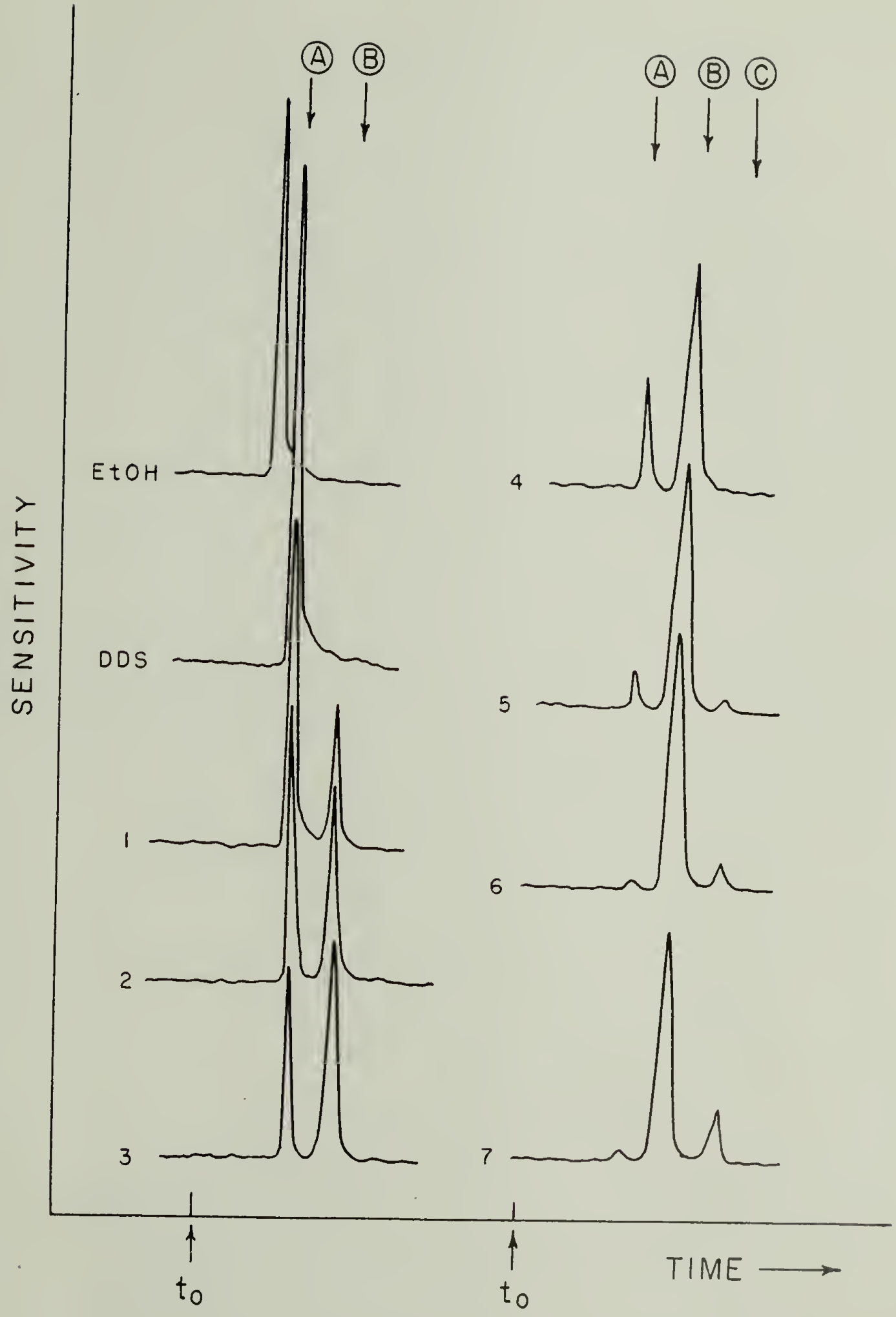


Figure 2-2. Fractionation of the reaction mixture from the preparation of dimethylethoxychlorosilane; see Table 2-1 for identity of the fractions indicated by the numbers.

TABLE 2-2

Composition of the Fractions Isolated from the Reaction Mixture in the Synthesis of Dimethylethoxychlorosilane

Fraction	Compound A, %	Compound B, %	Compound C, %
1	62	38	0
2	44	56	0
3	37	63	0
4	22	78	0
5	8.8	89.5	1.7
6	0.6	97.5	1.9
7	0.2	78.7	21.1

The ^{1}H NMR spectrum of this product contained the following peaks: $Si-CH_3$ (singlet) at δ = 0.25 ppm; $-CH_3$ (triplet) at δ = 1.10 ppm with J = 8 cps; $-CH_2-$ (quartet) at δ = 3.65 ppm with J = 8 cps and J´ = 9 cps.

2. Preparation of 4,4'-bis(dimethylethoxysilyl)phenyl ether (VIII)

This second step in the synthesis of ether-diol was performed according to the procedure described by Breed, Elliott and Whitehead[5,6].

A two-liter, three-necked, round-bottomed flask was equipped with a mechanical stirrer and a dry-ice condenser. The apparatus was assembled hot from the oven, throughly flamed under vacuum and flashed several times with dry nitrogen. When an inert atmosphere was achieved, a mixture of 54.25g (0.165 m) of bis(p-bromophenyl)ether, 50.06g (0.361 m) of dimethylethoxychlorosilane and 18.25g (0.79 m) of freshly cut sodium lamelae in 700 ml of diethyl ether was charged into the reaction flask. Stirring was started and the reaction mixture was allowed to reflux gently for 40 hours. As the reaction progressed the mixture changed from colorless to gray and finally to dark-blue. When the reaction was finished the mixture was filtered under inert atmosphere conditions and the filtrate was stripped of the solvent. The residue was fractionated by vacuum distillation, and fractions isolated at 0.15 mm are given in Table 2-3.

TABLE 2-3

Fractionation of the Reaction Mixture Resulting from Preparation of 4,4'-bis(dimethylethoxysilyl)phenyl ether

Fraction	Boiling Temperature, °C at 0.15 mm	Weight, g
1	<122	7.5
2	122-164	12.2
3	164-165	37.7
4	>165	3.8

Fraction 3 was 4,4'-bis(dimethylethoxysilyl)phenyl ether as shown by ^1H NMR spectrum which contained the following peaks: $Si-CH_3$ (singlet) at δ = 0.30 ppm; $-CH_3$ (triplet) at δ = 1.13 ppm with J = 8 cps; $-CH_2-$ (quartet) at δ = 3.65 ppm with J = 8 cps and J´ = 9 cps and $-C_6H_4-$ (two doublets) at δ = 7.10 ppm with J = 6 cps and at δ = 7.68 ppm with J = 6 cps. The compound was obtained in 61% yield, which is 5% more than reported[4]. The difference is probably due to the 16 hour longer reaction time allowed here.

3. Preparation of 4,4'-bis(dimethylhydroxysilyl) phenyl ether (II)

A solution of 48g of 4,4'-bis(dimethylethoxysilyl)phenyl ether (VIII) in 100 ml of absolute ethanol was added dropwise into a well-stirred solution of 19.4g of NaOH in 80 ml of CH_3OH and 15 ml H_2O. After one hour the mixture was treated with a solution of 19.4g NaOH in 80 ml of water and allowed to stir for another hour. The solution was then poured into 126g of KH_2PO_4 dissolved in 2 liters of an ice-water mixture and stored overnight. The crystallized product was filtered off, thoroughly washed with water and dried under reduced pressure. The crude material melted between 101 and 105°C. It was recrystallized from toluene and dried again to give 41g (85.4% yield) of the white, crystalline ether-diol (II) which melted at 104-105°C.

Anal. calcd. for $C_{16}H_{22}O_3Si_2$: C, 60.38%; H, 6.92%; Si, 15.09%. Found: C, 60.44%; H, 6.86%, Si, 15.11%.

The ^{1}H NMR spectrum obtained in deuterated dimethyl sulfoxide contained the following peaks: $Si-CH_3$ (singlet) at δ = 0.25 ppm; -OH (singlet) at δ = 5.88 ppm; $-C_6H_4-$ (two doublets) at δ = 7.10 ppm with J = 6 cps and at δ = 7.68 ppm with J = 6 cps, and it is shown in Figure 2-3.

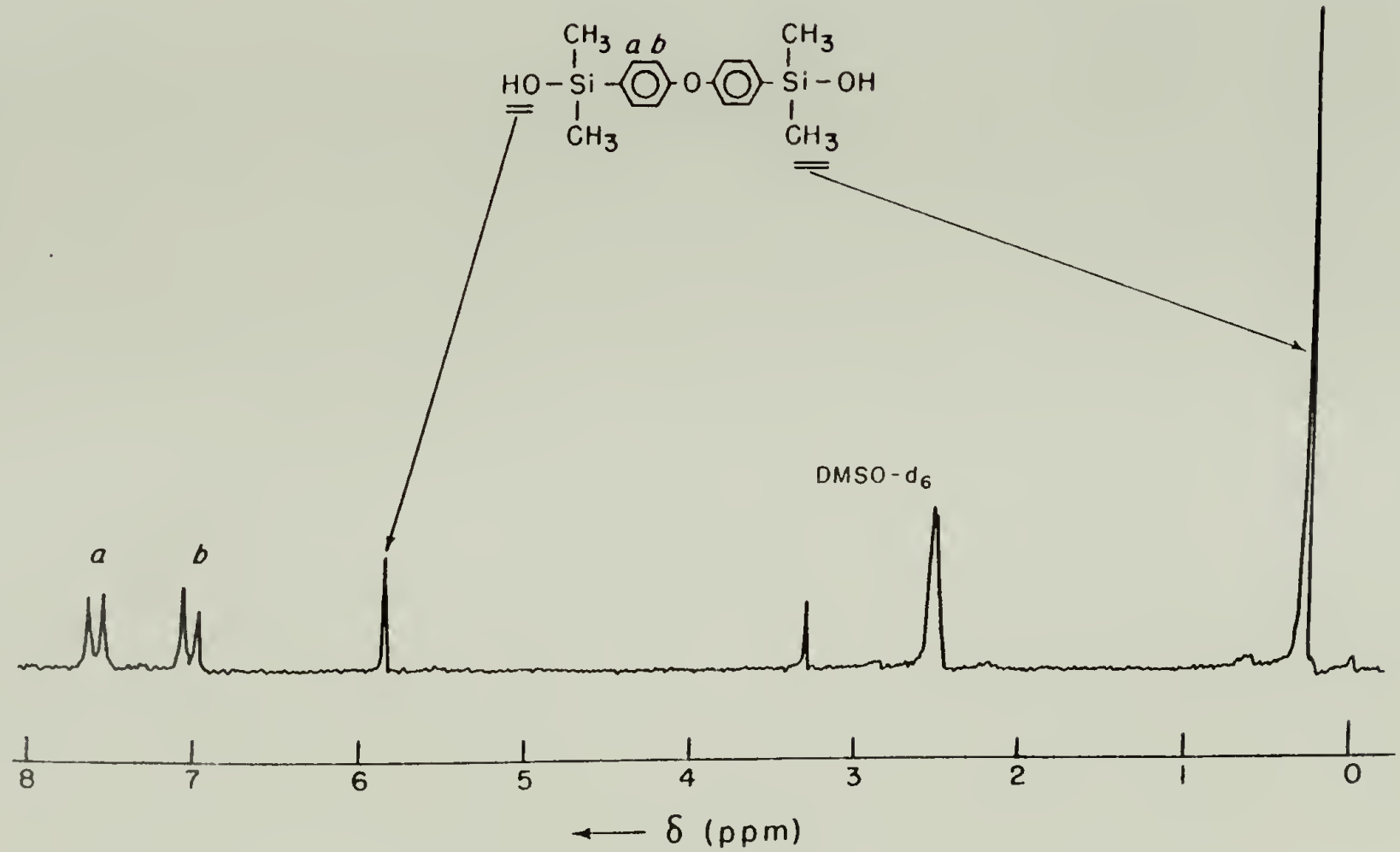


Figure 2-3. ^{1}H NMR spectrum of 4,4'-bis(dimethylhydroxysilyl)phenyl ether (ether diol) in deuterated dimethyl sulfoxide at 90 MHz.

Bibliography

1. W.R. Sorenson, T.W. Campbell, "Preparative Methods of Polymer Chemistry", Interscience, New York (1968), p. 187.

2. R.L. Merker, M.J. Scott, "Preparation and Properties of Poly-(tetramethyl-p-Silphenylene-Siloxane)", J. Polymer Sci., A-1, 2, 15 (1964).

3. N. Bilow, R.E. Lawrence, W.J. Patterson, "Synthesis and Polymerization of 1, 3-Bis-(2,3-epoxypropylphenyl)tetramethyl-disiloxanes and Related Compounds", J. Polymer Sci., A-1, 5, 2595 (1967).

4. "Organicum", Engl. Translation, Addison-Wesley Publishing Co., Inc. (1973), p. 675.

5. L.W. Breed, R.L. Elliott, M.E. Whitehead, "Arylene-Modified Siloxanes", J. Polymer Sci., A-1, 5, 2745 (1967).

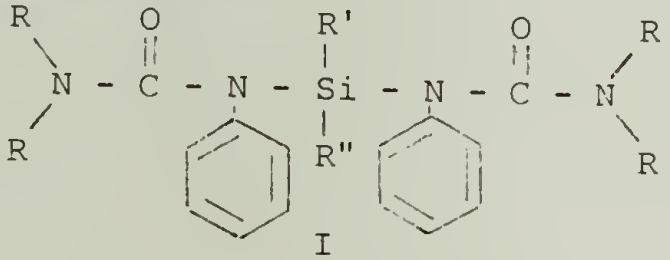
6. L.W. Breed, R.L. Elliott, "Arylenedisilanols", J. Organometal. Chem., 9, 188 (1967).

C H A P T E R I I I

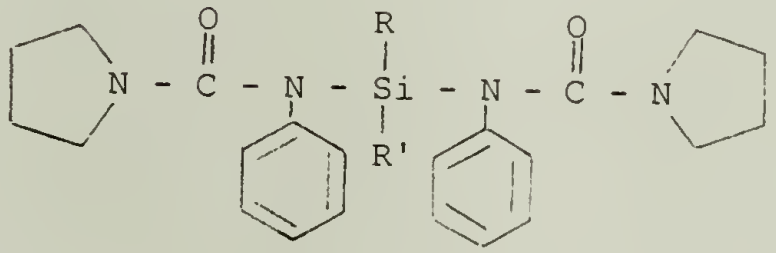
ON SYNTHESIS AND STABILITY OF BIS(1,1-TETRAMETHYLENE-3-PHENYLUREIDO)DIMETHYLSILANE

A. Introduction

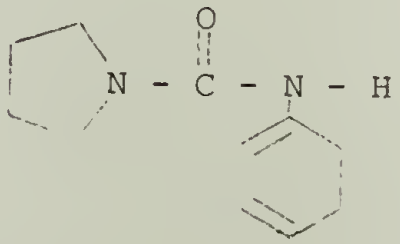
The general synthetic procedure used for the preparation of bis-(N-alkyl-N'-phenylureido)silanes (I) was reported in 1977 by Hedaya and coworkers[1]. Of the various derivatives described, the bis-N,N-tetramethylene derivative (II) was found to be the easiest to prepare in the purest state because of its ease of crystallization from the reaction mixture. However, even this derivative was not obtainable in a completely pure state, but it was always contaminated with N,N-tetramethylene-N'-phenyl urea (III).



I

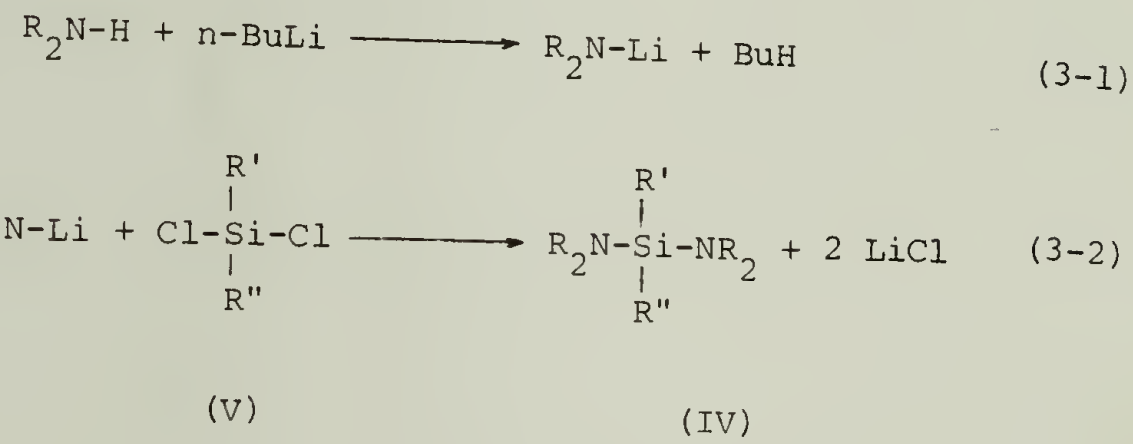


II

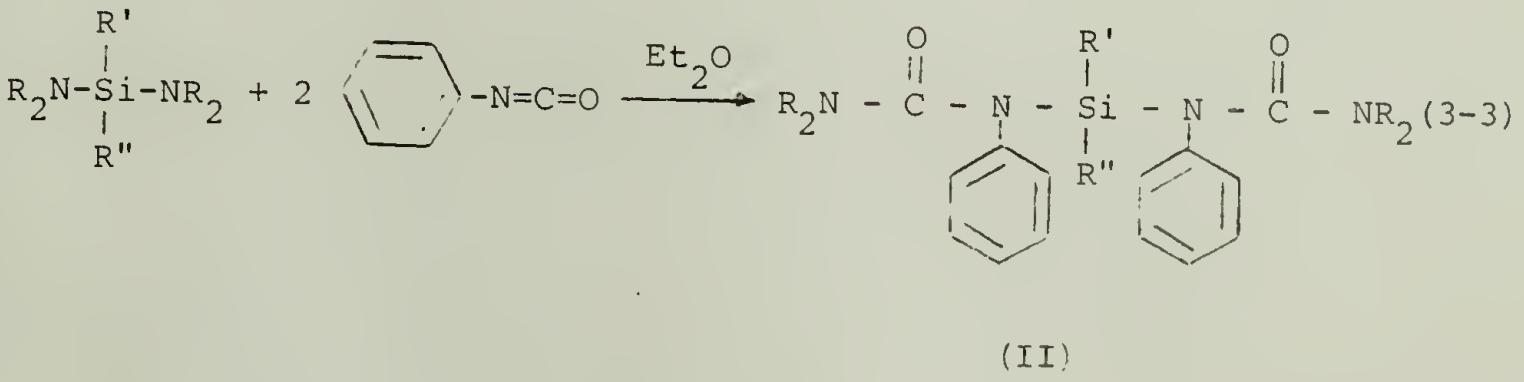


III

In order to prepare this bisureidosilane (II) in as high purity as possible the synthetic reaction conditions and stability of this compound under different storage conditions were examined in detail. The procedure described by Hedaya and coworkers started with the preparation of a silylamine (IV) from the corresponding dichlorosilanes (V) as follows:

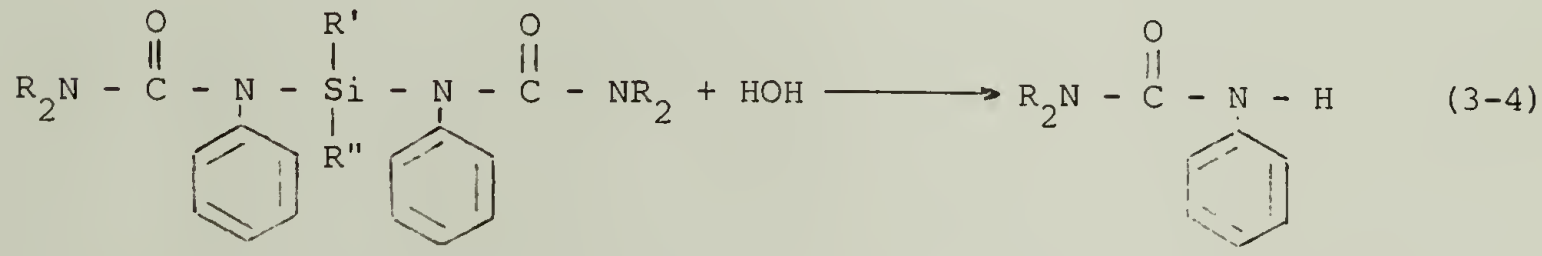


The amino derivative was converted into the bisureidosilanes (I) by an insertion reaction of phenyl isocyanate into the silicon-nitrogen bond, as follows:



The final step was performed in diethyl ether solution in which the bisureidosilane was insoluble and could be readily isolated by filtration.

By their chemical nature, however, bisureidosilanes are very reactive towards proton donating agents which easily attack the Si-N bond. This reactivity makes them very unstable, and they react with traces of water to form the corresponding urea, as follows:



(3-4)

This urea is poorly soluble in diethyl ether, and it also precipitates out of the reaction mixture, contaminating the products. Consequently, only in an absolutely dry reaction medium can pure bisureidosilane be prepared, and this degree of drying is not achieved in conventionally dried solvents[2].

To determine the purity of the bisureidosilanes prepared, as well as to follow the purification methods which were attempted, ^{1}H NMR spectroscopy was used to analyze the reagents and the products. Two approaches were attempted to prepare pure compounds: (1) purification of the urea-contaminated products and (2) optimization of the conditions employed in the insertion reaction 3-3. Once the pure bisureidosilane was prepared its long-term stability was investigated at different

conditions of atmosphere and temperature as described later in this chapter.

B. Preparation of Bisureidosilanes

1. Preparation of Bis(1,1-tetramethylene-3-phenylureido) dimethylsilane (VI)

a. Reagents

Pyrrolidine (Aldrich Chem. Co.) was heated for six hours over potassium hydroxide and distilled in a glass-ring column. The fraction which boiled at 87-88°C was collected, heated another 12 hours over potassium hydroxide and distilled again. The same procedure was repeated for a third time to yield a fraction with a sharp boiling point at 88°C. Dimethyldichlorosilane was purified by simple distillation, B.P. 70°C. Diethyl ether was refluxed over sodium lamelae (about 5 mm in diameter) for 12 hours and distilled. This procedure was repeated twice before a final 12 hour reflux and distillation over sodium and potassium was carried out. n-Butyllithium (Ventron; 2.4 M in n-hexane) was used without any further purification. Phenyl isocyanate (Aldrich Chem. Co.) was purified by vacuum distillation, and the fraction boiling at 30°C at 0.6 mm was used in reaction.

b. Procedure

The glass apparatus was assembled hot from the oven, flamed out under vacuum, and thoroughly purged with prepurified nitrogen.

750 ml of diethyl ether was placed into a three-necked, two-liter, round-bottomed flask equipped with mechanical stirrer, thermometer, dropping funnel, nitrogen atmosphere and dry-ice condenser. Inside a dry bag filled with nitrogen, a bottle of n-butyllithium in n-hexane, containing 1 mole of the reagent was emptied into the reaction flask. The apparatus was taken out of the dry bag and the solution was cooled in an ice-water bath, and 82 ml (0.997 m) of pyrrolidine were added dropwise over 3.5 hours. During this addition the solution was stirred continuously. As the reaction proceeded the liquid changed from clear-yellowish into cloudy-white, and it refluxed gently because of the exothermicity of the reaction.

The reaction mixture was protected from outside atmosphere by a strong stream of purging nitrogen and the dropping funnel used for adding pyrrolidine was replaced by another containing 59.7 ml (0.496 m) of dimethyldichlorosilane, which was added dropwise over a 4 hour reaction period. The mixture was well-stirred. A white precipitate immediately formed, and its amount increased as the reaction proceeded. After the addition of dimethyldichlorosilane was completed, the dropping funnel was removed, and the reaction mixture was slowly warmed to room temperature and allowed to stir overnight.

LiCl formed in the reaction was filtered with a sintered glass funnel under an inert atmosphere and the liquid phase was fractionated by distillation. The fractions obtained are indicated in Table 3-1.

Fraction 5 which represented bis(tetramethyleneamino)dimethylsilane was collected under nitrogen and with no further purification used in the next step.

TABLE 3-1

Distillation of the Reaction Product from the Synthesis of Bis(tetramethyleneamino)dimethylsilane

Number	Fraction	Temperature, °C	Quantity	Pressure
1	diethyl ether	34-36	730 ml	atmospheric
2	mixture of n-hexane and unreacted dimethyldichlorosilane	65-70	-	atmospheric
3	pyrrolidine	80-84	3 ml	atmospheric
4	pre-product	50-58	5 ml	0.6 mm
5	main cut	58-60	82 g	0.6 mm
6	residue	>60		0.6 mm

500 ml of dry diethyl ether were placed into 1 liter, three-necked flask equipped with a mechanical stirrer, dry-ice condenser, thermometer and maintained under nitrogen atmosphere. The apparatus was very carefully flamed under vacuum and purged with dry nitrogen several times. 81.6g (0.411 m) of bis(tetramethyleneamino)dimethylsilane, prepared in the way described above, were added to the solvent and the mixture was well stirred and cooled to the desired reaction temperature. Under a strong nitrogen purge a dropping funnel containing 89.4 ml (0.823 m; 97.97g) of freshly distilled phenyl isocyanate was attached to the reaction flask and the isocyanate was added dropwise. At the end of the addition, a white precipitate of bis(1,1-tetramethylene-3-phenylureido)dimethylsilane appeared. In some reactions, however, the precipitate would not form right away but would appear after overnight stirring of the reaction mixture. The ease with which the precipitate forms probably depended on the quantity of solvent used, that is, on the concentration of the resulting solution.

The reaction mixture was filtered under an inert atmosphere using a sintered-glass funnel to yield 153.1g (85.4%) of crude bisureidosilane. The product was washed with 1.5 l of prepurified diethyl ether (which had been distilled from n-butyllithium) and dried at room temperature under vacuum at 0.6 mm Hg for 48 hours.

2. Preparation of Bis(1,1-tetramethylene-3-phenylureido) methylvinylsilane

The synthetic procedure used was essentially the same as the one described above for the dimethyl derivative except for the replacement of dimethyldichlorosilane by methylvinyldichlorosilane, B.P. 92°C. Bis(tetramethyleneamino)methylvinylsilane was isolated as a clear colorless liquid boiling at 77°C at 1.4 mm Hg in an overall yield of 73.9%. Insertion of phenyl isocyanate into the silicon-nitrogen bond of the diamine as above lead to formation of methylvinyl ureidosilane derivative in 71% yield.

The purity of the two bisureidosilanes was determined by elemental analysis (Table 3-2), ^{1}H NMR spectroscopy and melting point (Table 3-3).

C. Purity of Bisureidosilanes

1. Determination of the Purity of Bisureidosilanes by ^{1}H NMR Spectroscopy

A 90 MHz Perkin Elmer ^{1}H NMR Spectometer, Model R-32, was used for this purpose. The samples were prepared in a dry-bag under an inert atmosphere of prepurified nitrogen in sealed tubes. Deuterated chloroform was used as a solvent.

The ^{1}H NMR spectra of bis(1,1-tetramethylene-3-phenylureido) dimethylsilane (VI) and 1,1-tetramethylene-3-phenylurea (III) (obtained by hydrolysis of VI by water) are shown in Figure 3-1, and the corresponding peak assignments are listed in Table 3-3.

TABLE 3-2

Elemental Analysis of Pure Bisureidosilanes and 1,1-tetramethylene-3-phenylurea

Compound		%C	%H	%N	%Si
dimethyl-bisureidosilane	calcd. for $C_{24}H_{32}O_2N_4Si$	66.05	7.34	12.84	6.42
	found	65.82	7.16	12.79	6.15
methylvinyl-bisureidosilane	calcd. for $C_{25}H_{32}O_2N_4Si$	66.96	7.14	12.50	6.25
	found	66.57	6.81	12.28	5.99
1,1-tetramethylene-3-phenylurea	calcd. for $C_{10}H_{14}ON_2$	69.47	7.37	14.74	
	found	69.44	7.48	14.73	

TABLE 3-3

Analysis of Pure Bisureidosilanes and 1,1-tetramethylene-3-phenylurea

Compound	T_m, °C	^{1}H NMR absorbtions: δ, ppm[a] Si-CH_3	$(-CH_2-)_2$	$(-CH_2-N-CH_2-)$	$-CH=CH_2$	N-H	Aromatic
dimethyl-bisureidosilane	132-133	0.98, s.	1.80, quin.	3.40, t.			7.20-8.00, mult.
methylvinyl-bisureidosilane	102-103	0.98, s.	1.66, quin.	3.36, t.	6.16, quar.		7.20-8.00, mult.
1,1-tetramethylene-3-phenylurea	131-132		1.98, quin.	3.65, t.		7.05, s. (broad)	

[a] In deuterated chloroform

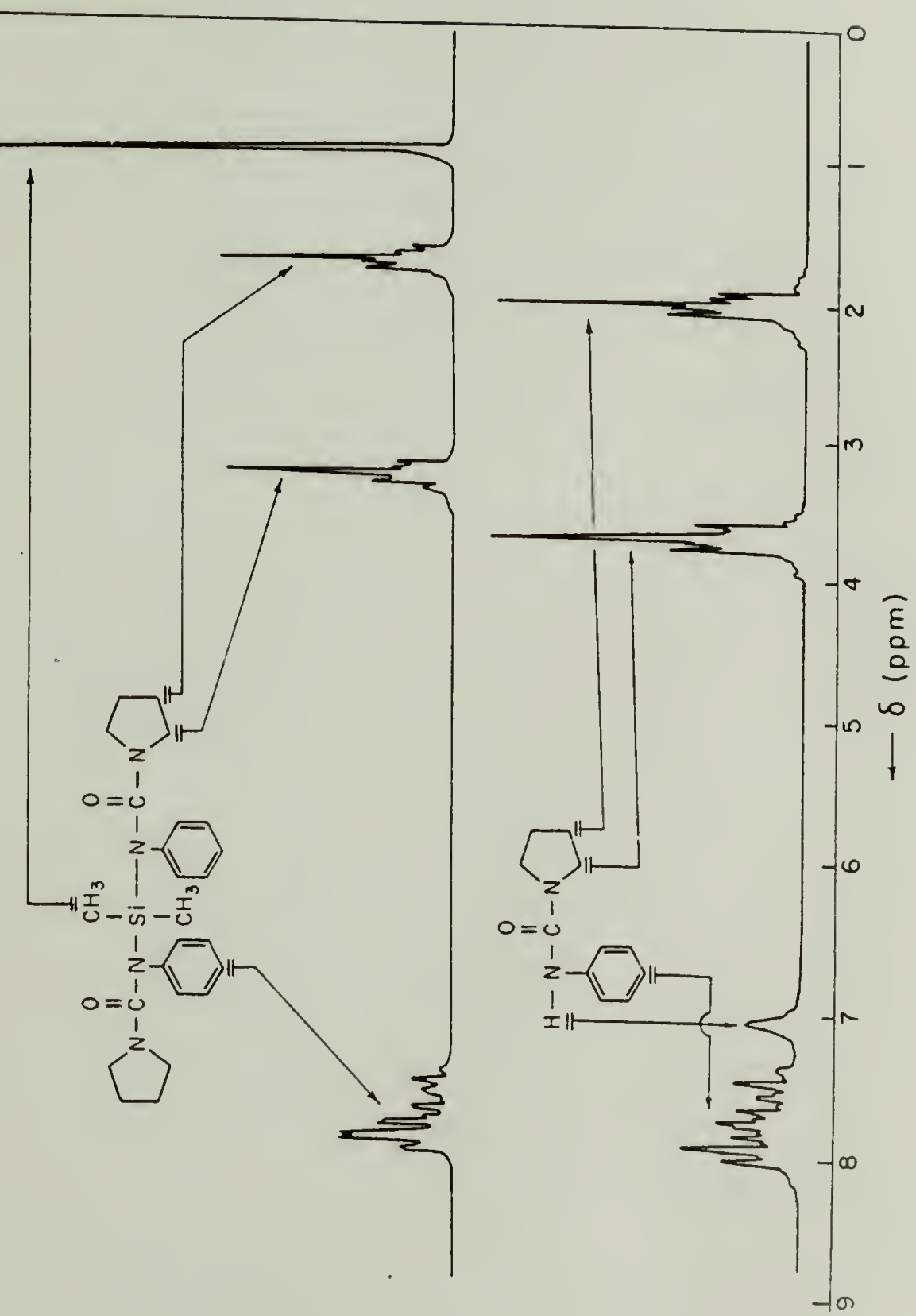
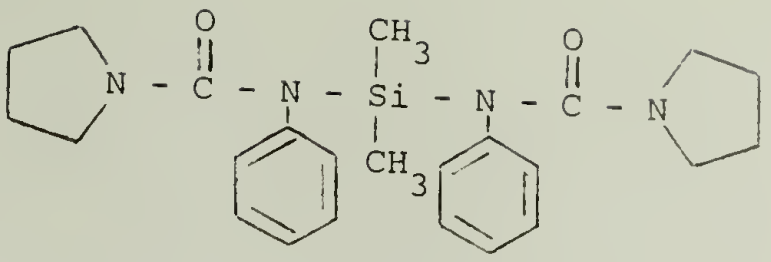
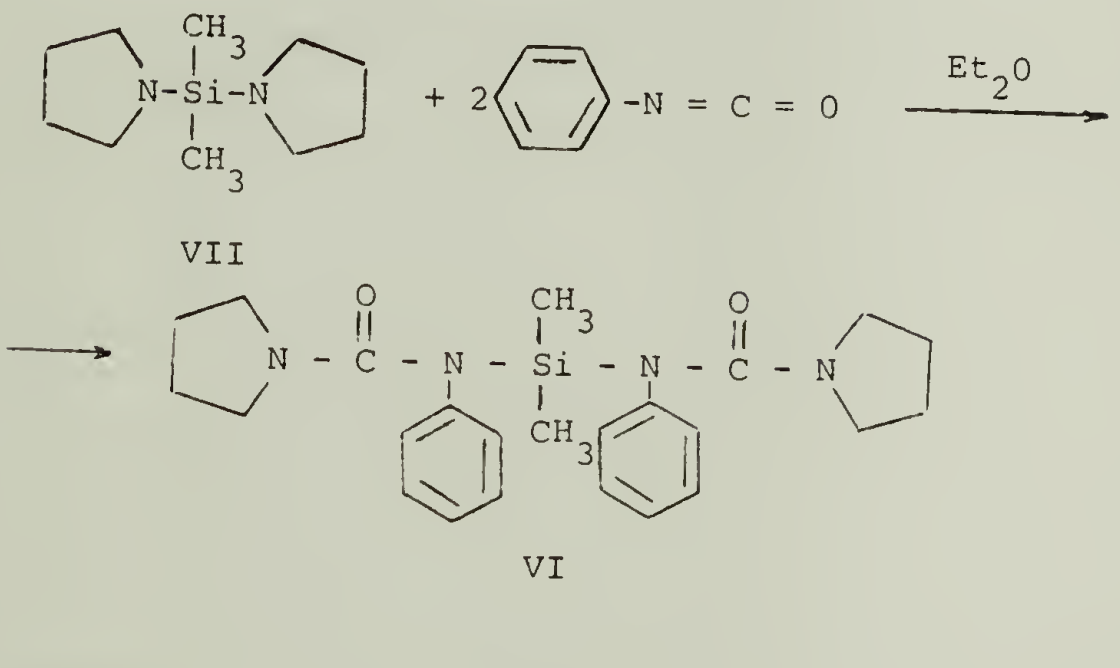


Figure 3-1. ^{1}H NMR spectra of pure bis(1,1-tetramethylene-3-phenylureido)-dimethylsilane and 1,1-tetramethylene-3-phenylurea in deuterated chloroform.

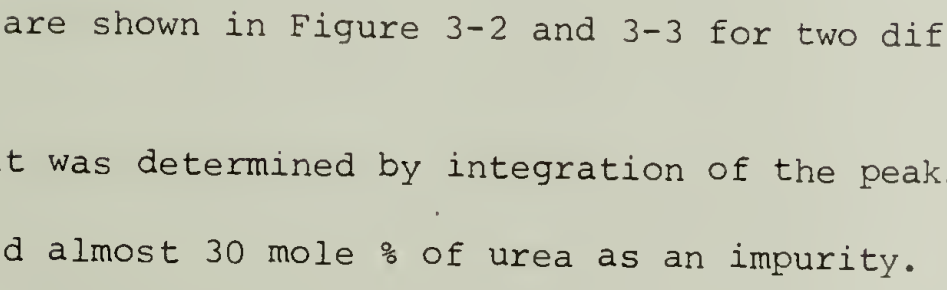


VI

Typical spectra obtained for bisureidosilane (VI) prepared at 0°C by the following reaction:



VII



VI

(3-5)

are shown in Figure 3-2 and 3-3 for two different solvents.

It was determined by integration of the peaks that the product contained almost 30 mole % of urea as an impurity. More important, however, ^1H NMR analysis proved to be a simple and reliable method to determine the purity of the ureidosilane and to follow its decomposition under a variety of storage conditions.

2. Purification of Urea-contaminated Bisureidosilanes

Several procedures were examined for purification of contaminated bisureidosilanes including: (1) extraction of urea from the sample

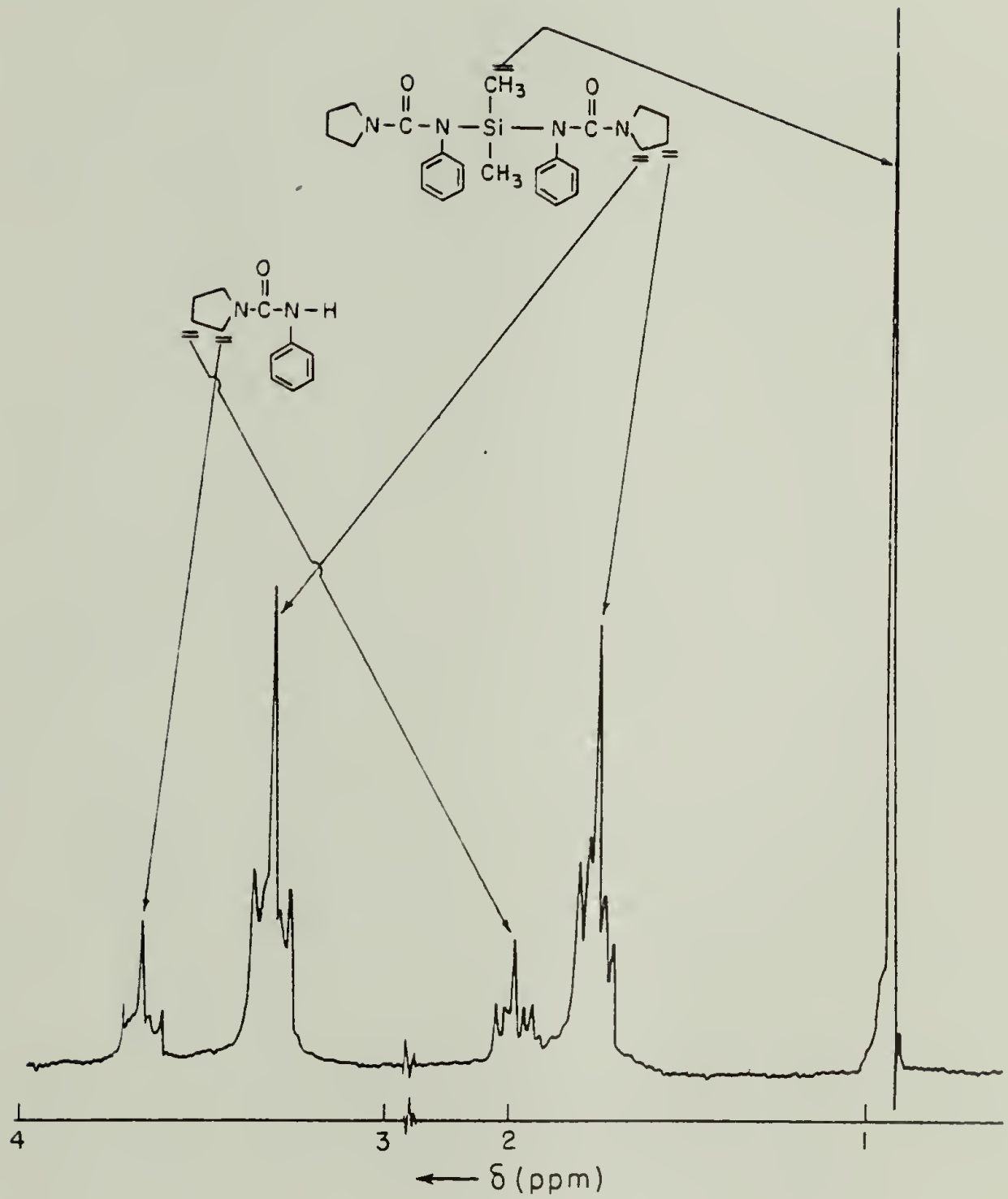


Figure 3-2. Typical ^{1}H NMR spectrum of bis(1,1-tetramethylene-3-phenylureido)dimethylsilane contaminated with 1,1-tetramethylene-3-phenylurea in deuterated chloroform.

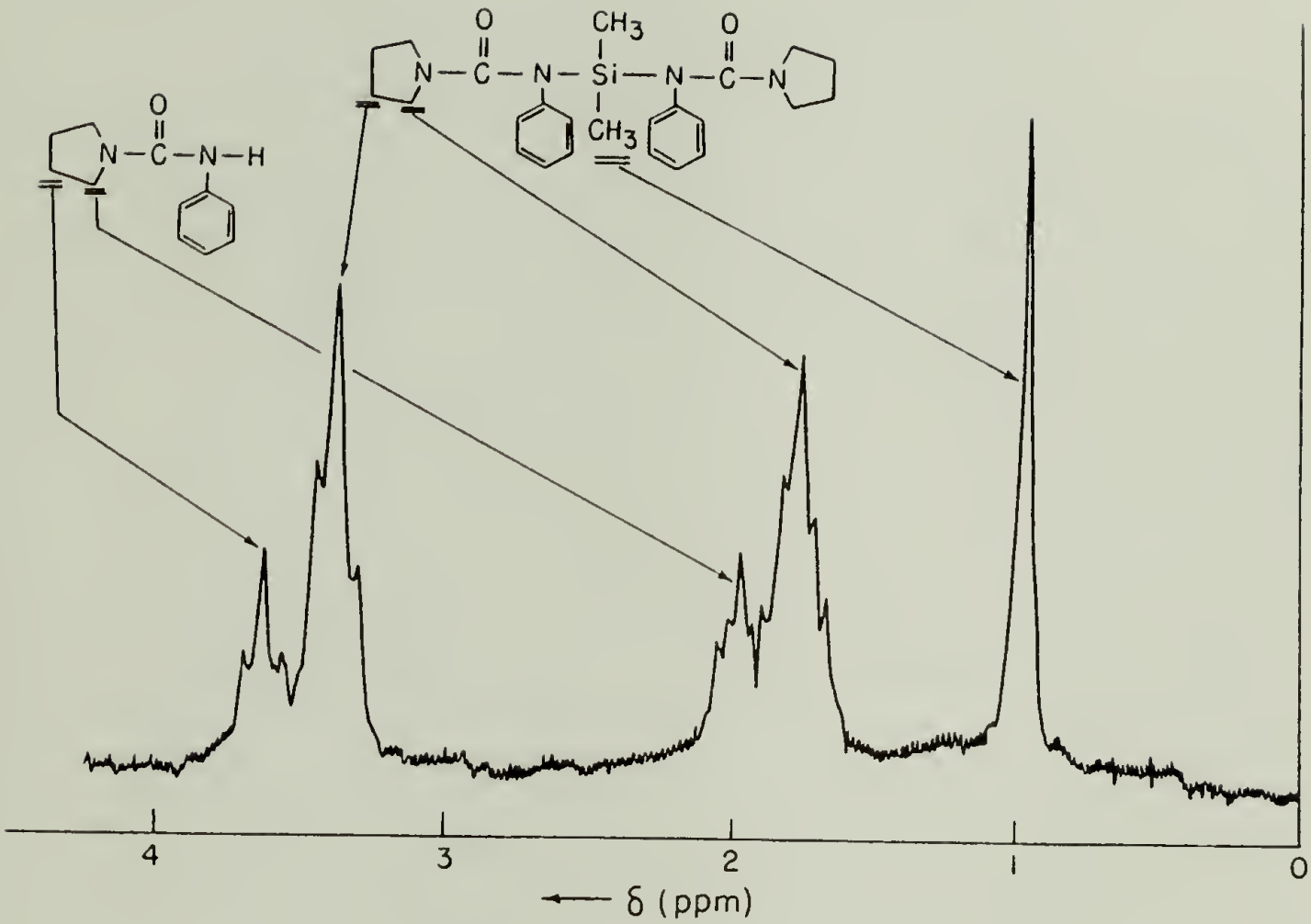


Figure 3-3. Typical ^{1}H NMR spectrum of bis(1,1-tetramethylene-3-phenylureido)dimethylsilane contaminated with 1,1-tetramethylene-3-phenylurea in chlorobenzene.

by diethyl ether under dry nitrogen; (2) recrystallization of the bisureidosilane from a tetrahydrofuran solution by diethyl ether; (3) recrystallization of the bisureidosilane from a chloroform solution by slow cooling; and (4) extraction of the bisureidosilane by chlorobenzene under a nitrogen atmosphere.

Unfortunately, none of these procedures was found to be of practical use. The first two led to a bisureidosilane contaminated with 5 to 10 mole % urea at best, most probably because of insufficient dryness of the ether solvent, which was dried according to the usual procedures[2]. The other two methods proved to be unsatisfactory for handling larger quantities of the bisureidosilane because of its high degree of solubility in both solvents. However, extremely pure compound was obtained by the first two procedures when the ether was distilled under nitrogen from a n-butyllithium solution directly into the flask containing the bisureidosilane.

3. Effect of the Reaction Temperature on Insertion Reaction of Phenyl Isocyanate into Bis(tetramethyleneamino)dimethylsilane

The bis(tetramethyleneamino)dimethylsilane (VII) which was reacted with phenyl isocyanate in Reaction 3-5 is a liquid which boils at 58-60°C at 0.6 mm Hg, and it can be obtained in high purity by careful vacuum distillation from the mixture resulting from Reaction 3-2. Hence, the insertion reaction is the purity controlling step in the synthesis of the bisureidosilanes. Alternatively, failure to purify the product by previously described methods also indicated that solvent

was a potential source of water which could react with the bisureido-silane after its formation by Reaction 3-4 to produce the urea-impurity. In any case, it was hoped that the lower reaction temperatures would decrease the rate of any side reaction and favor the preparation of the bisureidosilane in higher purity.

To determine the effect of reaction temperature on product purity a series of reactions was run at temperatures ranging from 0° to -30°C as indicated in Table 3-4. The measured temperature of the reaction mixture was accurate within 0.5°C. In all cases reaction time of 1 hour was allowed (from the beginning of phenyl isocyanate addition into a bis(tetramethyleneamino)dimethylsilane solution until the product was filtered out - see section B-1-b of this chapter). The purity of the products was determined by ^{1}H NMR spectroscopy (Section C-1). Table 3-5 lists the amounts of urea detected by integration of the spectra, and these results are plotted as a function of the reaction temperature in Figure 3-4.

These results show that purity of the bisureidosilanes depended greatly on the temperature at which phenyl isocyanate was inserted into the Si-N bond of the silyldiamine in Reaction 3-5. It was found that the purity increases with decreasing reaction temperature. For practical purposes a minimum reaction temperature of -20°C was sufficient to give extremely pure product.

TABLE 3-4

Effect of Reaction Temperature in the Synthesis of Bis(1,1-tetramethylene-3-phenylureido)dimethylsilane

Reaction Conditions		Silyalamine[a]		Phenyl Isocyanate[b]		Diethyl Ether	Yield
Temp., °C	Time, hours	g	mmole	g	mmole	ml	%
0	1	9.924	50.12	11.909	100.08	50.0	83.2
-5	1	9.882	49.93	11.905	100.04	50.0	84.6
-10	1	9.906	50.03	11.914	100.12	50.0	85.8
-21	1	9.853	49.76	11.769	98.90	50.0	85.0
-28	1	9.910	50.05	11.905	100.04	50.0	85.4

[a] Bis(tetramethyleneamino)dimethylsilane

[b] Density 1.096 g/ml

TABLE 3-5

Amount of 1,1-tetramethylene-3-phenylurea as Detected by ^{1}H NMR Spectroscopy in Bis(1,1-tetramethylene-3-phenylureido)dimethylsilane Synthesized at Different Reaction Temperatures

Reaction Temperature, °C	I_{urea}	$I_{bisureidosilane}$	Urea Present, mole%
0	32	68	32
-5	10.5	89.5	10.5
-10	4.5	95.5	4.5
-21	1	99	1
-28	0	100	0

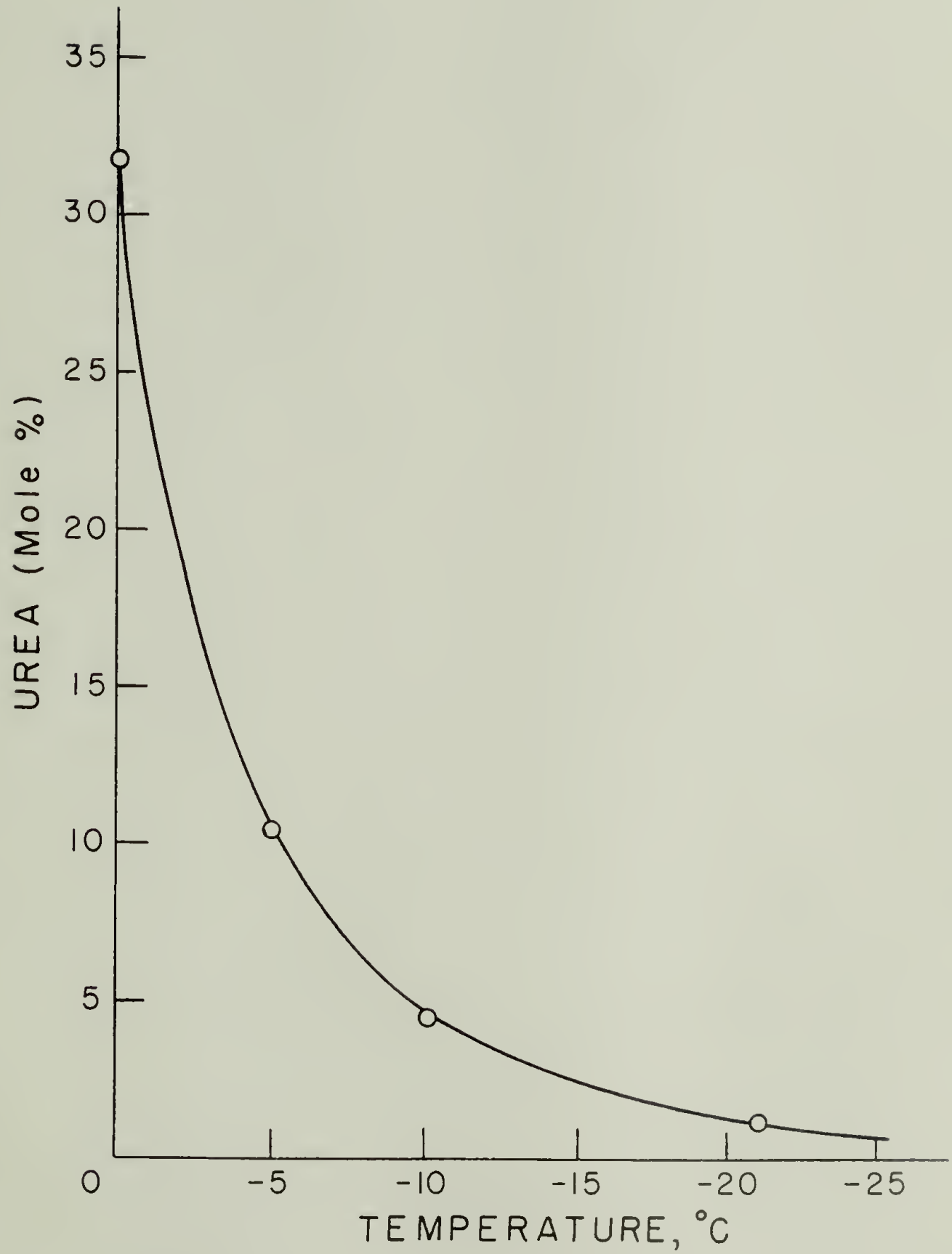


Figure 3-4. Amount of 1,1-tetramethylene-3-phenylurea in bis(1,1-tetramethylene-3-phenylureido)dimethylsilane as a function of reaction temperature.

D. Stability of Bisureidosilanes

The stability of pure bis(1,1-tetramethylene-3-phenylureido) dimethylsilane was examined in order to establish the best conditions for storage. In each of the experiments 5g of urea-free bisureido-silane were placed within a dry bag filled with nitrogen into a 50 ml one-necked, round-bottomed flask and the samples were exposed to the following conditions:

(1) air at room temperature: in an opened flask on a bench top;

(2) vacuum at -5°C: in an evacuated flask closed with a stopper and stored in a refrigerator;

(3) nitrogen at room temperature: under a positive pressure of nitrogen in a flask stored in a desiccator which was also filled with nitrogen; and

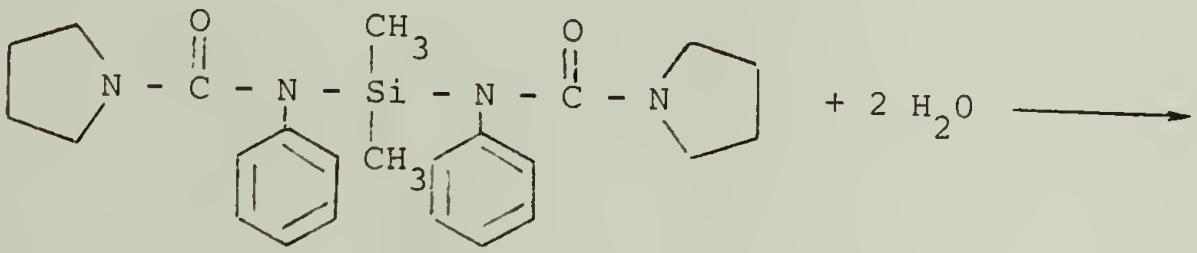
(4) nitrogen at -20°C: in a flask under nitrogen atmosphere stored in a freezer.

During the initial stages of the experiments, samples were taken every day and analyzed for their urea content by ^{1}H NMR. Later, it was done at weekly intervals.

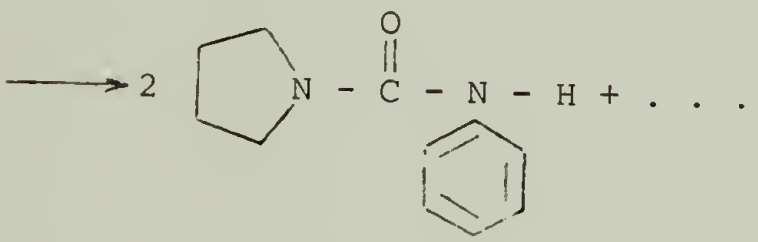
With the exception of the sample of bisureidosilane exposed to air all solutions for ^{1}H NMR analysis were prepared in a dry bag under nitrogen atmosphere. The solid compound was dissolved in deuterated chloroform and injected into an NMR tube filled with nitrogen and the tube was carefully sealed. The amount of urea formed on storage was determined by integration of the peaks at δ = 1.98 ppm and δ = 3.65 ppm

for urea and the peaks at δ = 1.80 ppm and δ = 3.40 ppm for bisureidosilane (see Table 3-3 and Figure 3-2). The average of these values was used in the calculations of the results in Table 3-6 and Figure 3-5.

On the basis of data presented in Table 3-6 calculations indicate that the conversion of the bisureidosilane to the urea followed pseudo-first order kinetics as shown in Tables 3-7 through 3-10 and in Figure 3-6. The reaction involved is presumed to be a hydrolysis with water impurity, as follows:



(US)



(U) (3-6)

According to this proposed reaction each molecule of bisureidosilane yields two molecules of urea. The general rate expression for Reaction 3-6 is[3]:

$$-\frac{d\,[US]}{dt} = k \cdot [US] \cdot [H_2O]^2 \qquad (3\text{-}7)$$

If the water concentration is kept constant or if it is either too large or too small compared to the concentration of the bisureidosilane, an apparent first-order rate constant k' could be calculated as follows[3]:

TABLE 3-6

Amount of 1,1-tetramethylene-3-phenylurea Formed in Samples of Bis-(1,1-tetramethylene-3-phenylureido)dimethylsilane

Time, days	Urea Content After Storage Conditions, mole %			
	Air at room T	Vacuum at -5°C	N_2 at room T	N_2 at -20°C
3	10	1.5	-	-
7	32	3.5	1.5	0.5
11	50	-	-	-
14	64	5.5	3	1
28		10.5	5	2
42		-	7.5	-
48	16	-	2.5	
56	23	9	6	
70	27	11.5	6.5	
84	32	-	-	
98	38	19	9	

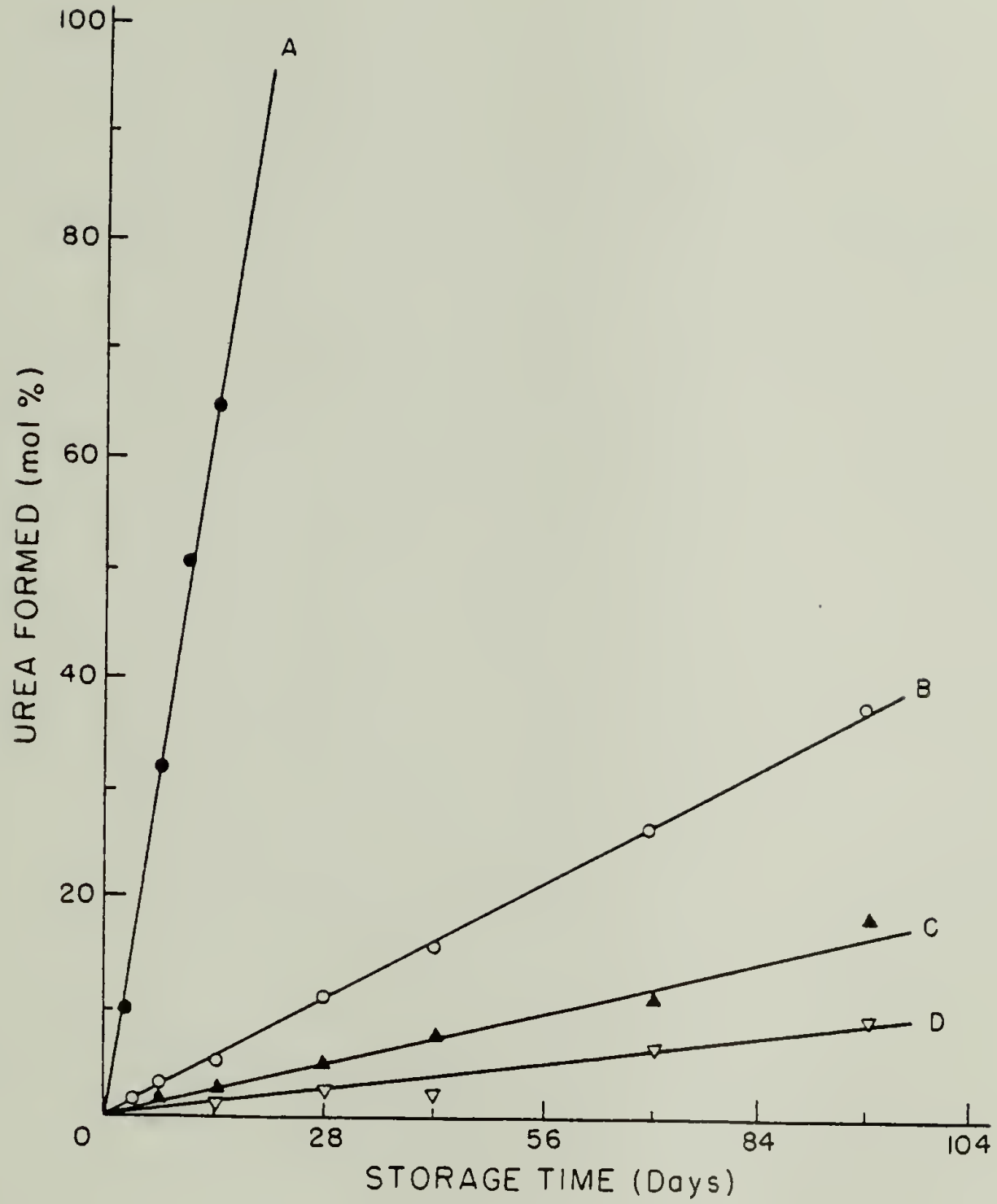


Figure 3-5. Formation of 1,1-tetramethylene-3-phenylurea from bis(1,1-tetramethylene-3-phenylureido)dimethylsilane under the following storage conditions: (A) air at room temperature; (B) vacuum at -5°C; (C) nitrogen at room temperature; and (D) nitrogen at -20°C.

TABLE 3-7

Determination of Apparent First Order Rate Constant, k', for Hydrolysis of Bis(1,1-tetramethylene-3-phenylureido)dimethylsilane in Air at Room Temperature

Iu/Ius[a]	[US], mole %	Time, days	$\ln \frac{[US]_o}{[US]}$	$k' \times 10^2$, $days^{-1}$
0/100	100	0		
10/90	81.8	3	0.201	6.70
32/68	51.5	7	0.664	9.48
50/50	33.3	11	1.10	9.99
64/36	21.9	14	1.57	10.8

$$k'_{av.} = 9.25 \times 10^{-2} \text{ days}^{-1}$$

$$k'_{av.} = 3.85 \times 10^{-3} \text{ hours}^{-1}$$

[a] The ratio Iu/Ius in Tables 3-7 through 3-10 represents the average of the ratios of the integrals obtained for the urea and bisureidosilane peaks in the ^1H NMR spectra.

TABLE 3-8

Determination of Apparent First Order Rate Constant, k', for Hydrolysis of Bis(1,1-tetramethylene-3-phenylureido)dimethylsilane in Vacuum at -5°C

Iu/Ius	[US], mole %	Time, days	$\ln \frac{[US]_o}{[US]}$	$k' \times 10^3$, $days^{-1}$
0/100	100	0		
1.5/98.5	97.04	3	0.030	10.0
3.5/96.5	93.24	7	0.069	9.9
5.5/94.5	89.57	14	0.110	7.9
10.5/89.5	81.0	28	0.211	7.5
16/84	72.41	48	0.323	6.7
23/77	62.6	56	0.468	8.4
27/73	57.48	70	0.554	7.9
32/68	51.52	84	0.663	7.9
38/62	44.93	98	0.800	8.2

$k'_{av.} = 8.05 \times 10^{-3}$ $days^{-1}$

$k'_{av.} = 3.35 \times 10^{-4}$ $hours^{-1}$

TABLE 3-9

Determination of Apparent First Order Rate Constant, k', for Hydrolysis of Bis(1,1-tetramethylene-3-phenylureido)dimethylsilane in Nitrogen at Room Temperature

Iu/Ius	[US], mole %	Time, days	$\ln \frac{[US]_o}{[US]}$	$k' \times 10^3$, $days^{-1}$
0/100	100	0		
1.5/98.5	97.04	7	0.030	4.29
3/97	94.18	14	0.051	3.64
5/95	90.48	28	0.100	3.57
7.5/92.5	86.05	42	0.150	3.58
9/91	83.49	56	0.180	3.22
11.5/88.5	79.37	70	0.231	3.30
19/81	68.07	98	0.385	3.92

$k'_{av.} = 3.65 \times 10^{-3}$ $days^{-1}$

$k'_{av.} = 1.52 \times 10^{-4}$ $hours^{-1}$

TABLE 3-10

Determination of Apparent First Order Rate Constant, k', for Hydrolysis of Bis(1,1-tetramethylene-3-phenylureido)dimethylsilane in Nitrogen at -20°C

Iu/Ius	[US], mole %	Time, days	$\ln \frac{[US]_o}{[US]}$	$k' \times 10^3$, $days^{-1}$
0/100	100	0		
0.5/99.5	99.01	7	0.0099	1.41
1/99	98.02	14	0.0199	1.42
2/98	96.08	28	0.0399	1.42
2.5/97.5	95.12	48	0.0500	1.04
6/94	88.68	56	0.1201	2.14
6.5/93.5	87.79	70	0.1302	1.86
9/91	83.49	98	0.1804	1.84

$k'_{av.} = 1.68 \times 10^{-3}$ $days^{-1}$

$k'_{av.} = 7.0 \times 10^{-5}$ $hours^{-1}$

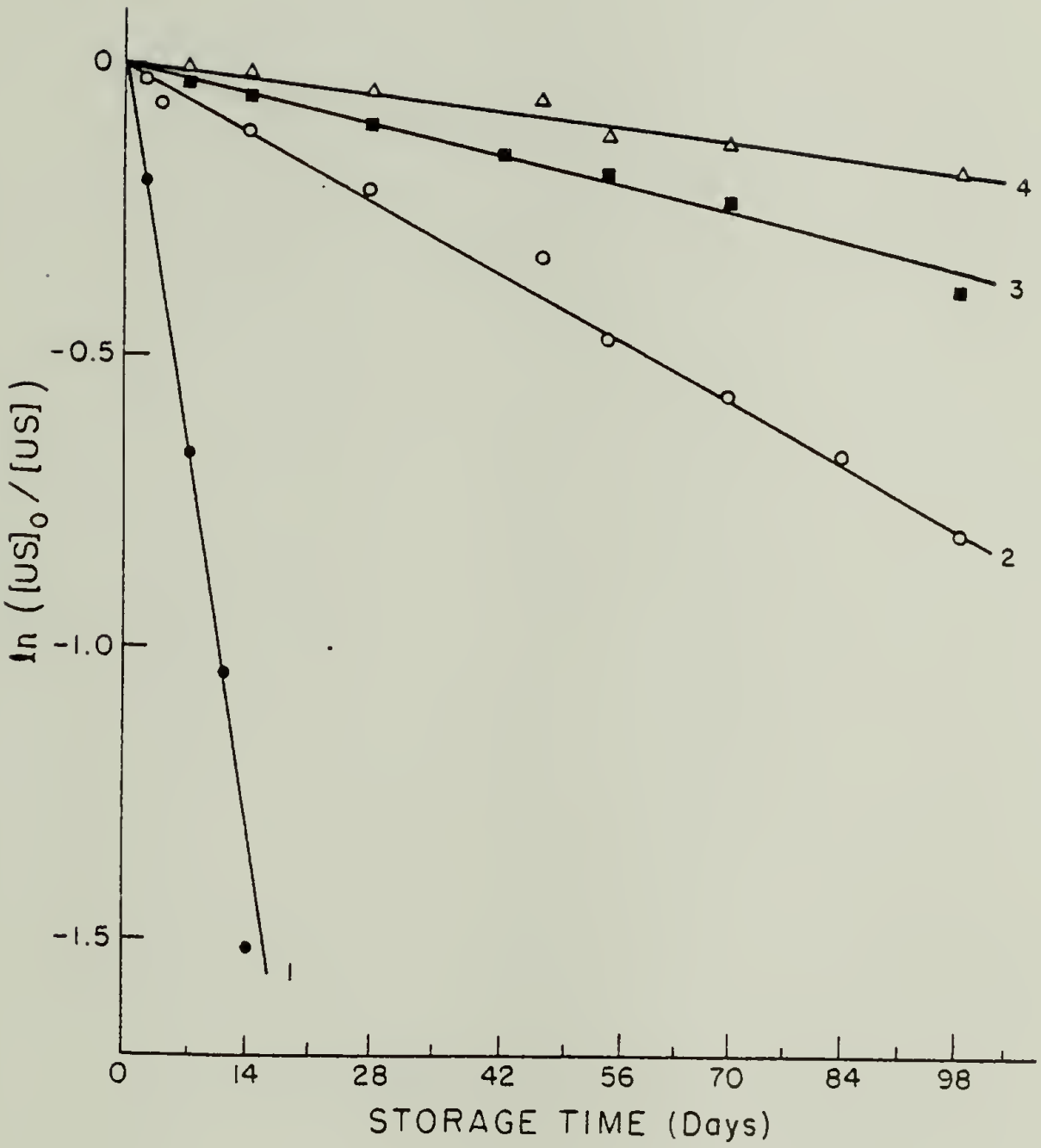


Figure 3-6. Rate of hydrolysis of bis(1,1-tetramethylene-3-phenylureido)dimethylsilane under the following storage conditions: (1) air at room temperature; (2) vacuum at -5°C; (3) nitrogen at room temperature; (4) nitrogen at -20°C.

TABLE 3-11

Average Apparent First-Order Rate Constants, k', for the Hydrolysis of Bis(1,1-tetramethylene-3-phenylureido)dimethylsilane Under Various Storage Conditions

Atmosphere	Temperature, °C	k', $days^{-1}$	k', $hours^{-1}$
air	room	9.25×10^{-2}	3.85×10^{-3}
vacuum	-5	8.05×10^{-3}	3.35×10^{-4}
nitrogen	room	3.65×10^{-3}	1.52×10^{-4}
nitrogen	-20	1.68×10^{-3}	7.0×10^{-5}

$$k' = k \cdot [H_2O]^2 \qquad (3\text{-}8)$$

$$-\frac{d[US]}{dt} = k' \cdot [US] \qquad (3\text{-}9)$$

Plots of ln ($[US]_0/[US]$) vs. time for each of the storage conditions are given in Figure 3-6. These plots show a relatively good straight line behavior. The apparent first order rate constants calculated for each set of storage conditions are given in Tables 3-7 through 3-10 and summarized in Table 3-11.

E. Conclusions

The following conclusions can be drawn from the results collected in the Figures and Tables of this chapter:

(1) It is confirmed that the method for preparation of bisureidosilanes described by Hedaya and coworkers[1] is useful for synthesis of these compounds.

(2) The major problem involved in the synthesis was contamination of the product by the unsymmetrical urea impurity. The content of this impurity in the crude reaction product depended on the conditions under which the final insertion reaction of phenyl isocyanate into the silyldiamine was performed. Reaction temperature was a very important variable, and the lower the temperature the purer the product obtained. At reaction temperatures below -20°C no detectible amounts of urea impurity were present.

(3) It was very difficult to purify contaminated bisureidosilanes in a practical way because of their pronounced sensitivity towards moisture.

(4) ^{1}H NMR spectroscopy was a good method for determination of the purity of the bisureidosilanes.

(5) Long-term stability of the bisureidosilanes was tested under different storage conditions. In all cases bis(1,1-tetramethylene-3-phenylureido)dimethylsilane decomposed at finite rates, but decomposition was the slowest under nitrogen and at -20°C. For all of the conditions tested, the hydrolysis reaction appeared to follow pseudo-first order kinetics. These experiments suggest that if the bisureidosilanes are carefully stored these compounds can be kept pure during at least limited time periods. But, even under the most favorable storage conditions found significant decomposition occurred within three months.

Bibliography

1. E. Hedaya, J.H. Kawakami, P.W. Kopf, G.T. Kwiatkowski, D.W. McNeil, D.A. Owen, E.N. Peters, R.W. Tulis, "D_2-meta-Carborane-Siloxanes. IV. Synthesis of Linear, High Molecular Weight Polymers", J. Polymer Sci., Polymer Chem. Ed., 15, 2229 (1977).

2. D.R. Burfield, K. Lęe, R.H. Smithers, "Desiccant Efficiency in Solvent Drying. A Reappraisal by Application of a Novel Method for Solvent Water Assay", J. Org. Chem., 42, 3060 (1977).

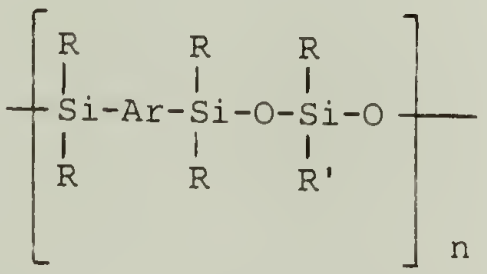
3. A.A. Frost, R.G. Pearson, "Kinetics and Mechanism", second edition, John Wiley and Sons, Inc. (1961).

C H A P T E R I V

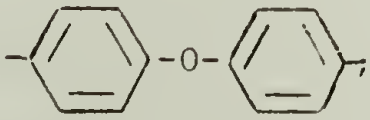
PREPARATION OF EXACTLY ALTERNATING SILARYLENE-SILOXANE POLYMERS BY CONDENSATION POLYMERIZATION OF ARYLENEDISILANOLS AND BISUREIDOSILANES

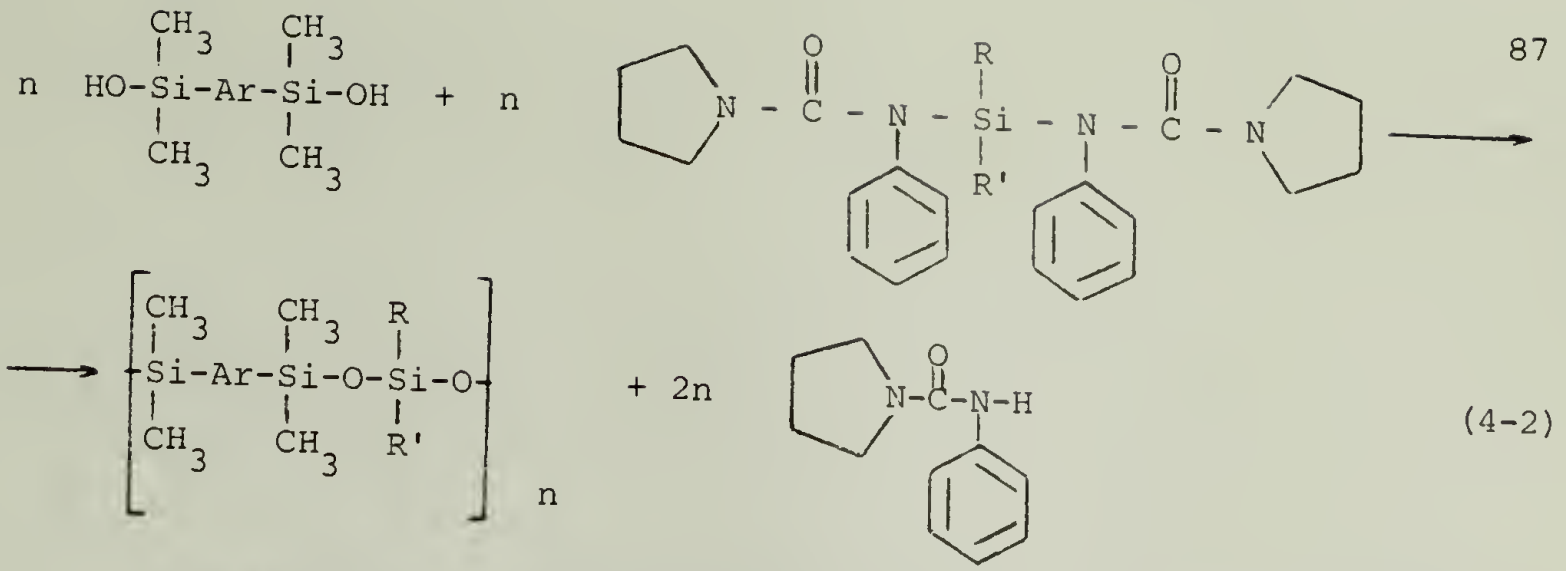
A. Introduction

Exactly alternating silarylene-siloxane polymers of the following general formula:



(4-1)

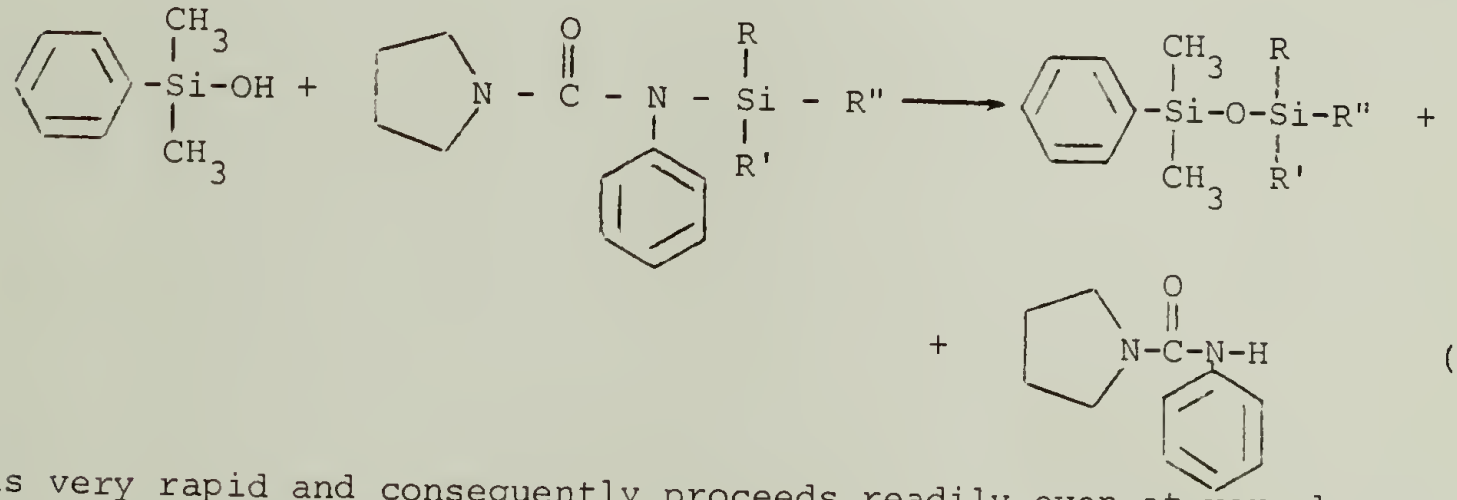
where: Ar =  or  ; R = $-CH_3$; and R' = $-CH_3$ or $-CH = CH_2$, were prepared using the reaction previously developed for the preparation of alternating carborane-siloxane polymers by Hedaya and coworkers[1]. This reaction is a condensation polymerization in which the arylenedisilanols and reactive bisureidosilanes are combined to form poly(silarylenesiloxanes) and an asymmetrical urea by-product, as follows:



(4-2)

This synthetic route was chosen because of its several promising characteristics including the following:

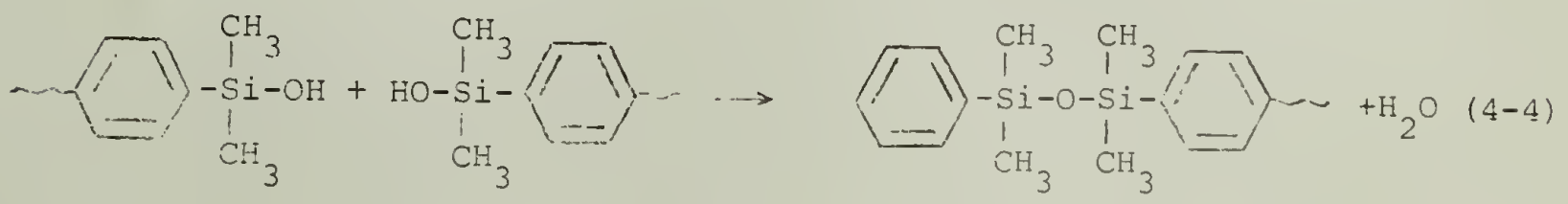
(1) The nucleophilic substitution of bisureidosilane by a silanol, which is the basic reaction involved as shown below:



(4-3)

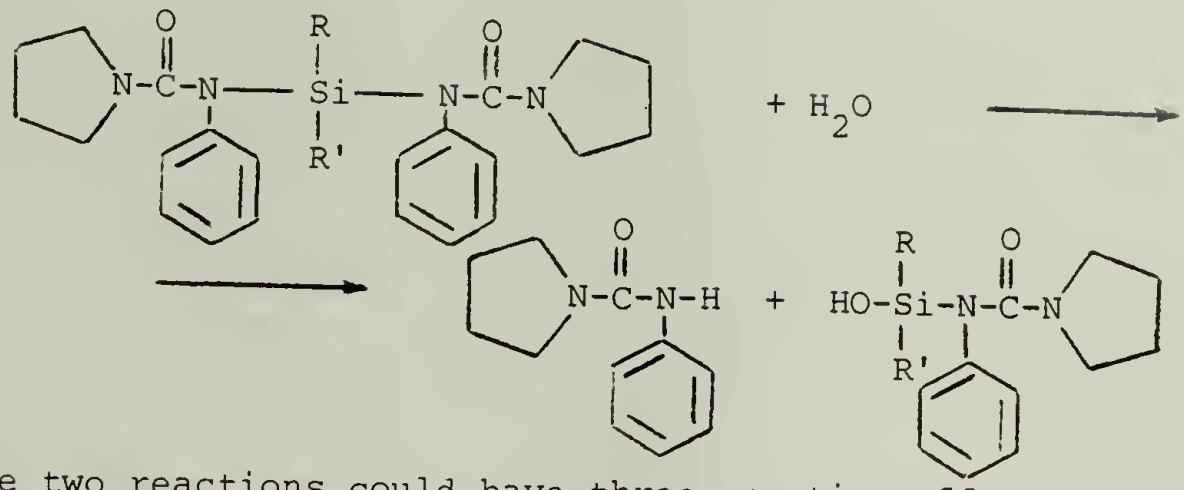
is very rapid and consequently proceeds readily even at very low temperatures.

(2) The use of low reaction temperatures is very important in this polymerization because they prevent, or at least slow down, possible diol self-condensation reactions shown below, which, if present, would destroy the alternating character of the polymer and unbalance the functional groups present:



(4-4)

Water formed in this reaction could also react with the bisureidosilanes as follows:



(4-5)

These two reactions could have three negative effects on the properties of the polymers formed. Firstly, introduction of rigid -Ar-Si-O-Si-Ar- units into the polymer instead of the more flexible -Ar-Si-O-Si-O-Si-Ar- would increase the glass transition temperatures of the products. Secondly, formation of monofunctional silanols through Reaction 4-5 would introduce an A-B type monomer into A-A + B-B type condensation system which, if itself-condensed, could possibly affect molecular weight distribution of the polymers obtained and thirdly, the Ar-Si-O-Si-Ar units introduced into the polymers would be sites of decreased thermal stability.

(3) A very attractive feature of this reaction system is the formation of an unsymmetrical urea. This compound is neutral and unreactive towards Ar-Si groups. Consequently, chain scission by the attack of the leaving group on the Ar-Si polymer linkages would not occur as it does when bisamino or biscarbamato monomers are used[1]. Such reactions can prevent the formation of high molecular weight polymers.

(4) Extremely high water sensitivity of bisureidosilanes necessitates that the following reaction conditions be used:

a) an extremely dry atmosphere of an inert gas in the polymeriza-

tion reactor, and

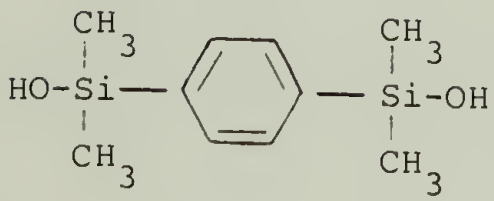
b) a very dry reaction solvent.

(5) The reaction is carried out in chlorobenzene solvent. Chlorobenzene is chosen, firstly because it is a good solvent for polymers but a non-solvent for urea, causing precipitation of the latter as the reaction proceeds. This precipitation becomes an additional driving force for the condensation polymerization, and it also enables a very easy separation of the polymer after completion of the reaction by simple filtration of the by-product. Secondly, chlorobenzene is also a good solvent for bisureidosilanes and simplifies their addition. Thirdly, once dried, chlorobenzene can be kept moisture free with reasonable precautions such as storing over CaH_2 and under dry nitrogen. Fourthly, chlorobenzene absorbs in the ^1H NMR spectrum at δ = 7.20 ppm and does not interfere with any other significant absorption peak of the components of the reaction mixture, and also it can be used for the internal locking signal. Finally, it is miscible with tetrahydrofuran which permits the direct use of GPC for monitoring the condensation polymerization.

On the basis of these characteristics, this reaction was used in an attempt to prepare a new series of exactly alternating silarylene-siloxane polymers, and the possibilities for modification of the backbone using different arylenedisilanols and bisureidosilanes were investigated.

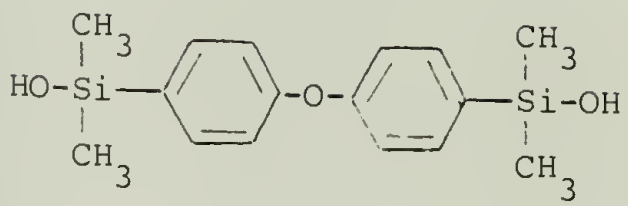
B. Monomers

The monomers used in this work include the following:



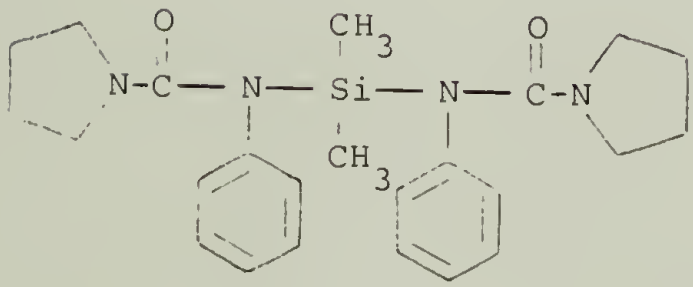
I

p-diol



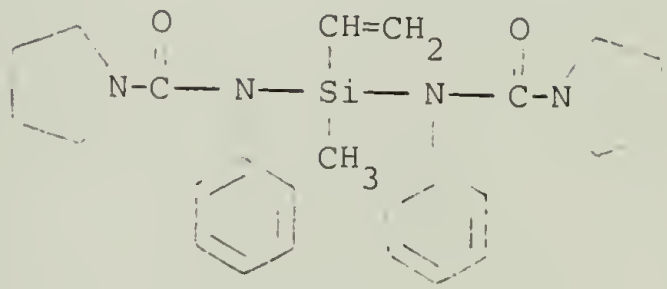
II

ether diol



III

dimethylureidosilane



IV

methylvinylureidosilane

C. Monitoring of the Condensation Polymerization by ^{1}H NMR Spectroscopy

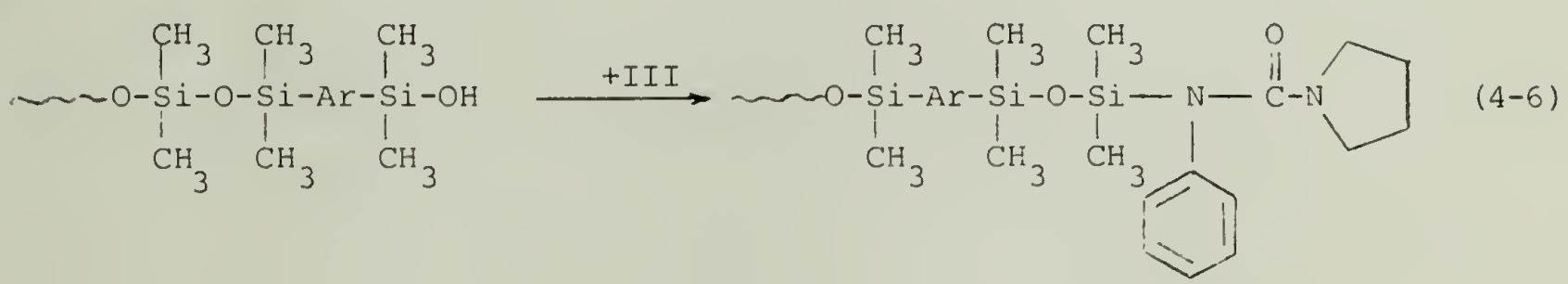
1. General

The successes achieved in determining the purity and stability of the bisureidosilanes as described in Chapter III suggested the use of ^{1}H NMR to monitor the condensation polymerization reaction in an attempt to overcome the usual problems involved in obtaining high molecular weights, i.e.: the necessity for high conversions and for conditions of exact stoichiometric equivalence[2].

The polymerization reaction was very fast for all monomers used. For example, when a fractional equivalent of bisureidosilane was added to a sample of the polymerization mixture containing an excess of silanol functional groups, the ^{1}H NMR spectrum which was taken only about 10 min later showed that all of the ureidosilane was consumed. This very high rate of reaction permitted the use of a wide variety of reaction conditions, and suggested that the reaction could be run at very low temperatures, the significance of which was discussed earlier. In general, the condensation polymerization reaction could be monitored by ^{1}H NMR by any of the following ways: (1) by following the disappearance of either monomer as they reacted and by observing the presence of unreacted functional group which was in excess after the equimolar ratio had been reached; (2) by following the appearance of the by-product; or (3) by following the disappearance of end-functional groups on the growing polymer chains as the degree of polymerization increased and

the concentration of the end-groups correspondingly decreased and ultimately disappeared.

After careful examination and evaluation of these methods, it seemed most practical to use the first one. If the condensation polymerization was started with a large excess of disilanol monomer over ureidosilane (i.e.: r = [diol]/[ureidosilane] > 1) the growing chains all had hydroxyl end groups. To join those oligomers together into longer chains, more ureidosilane had to be added. After equimolarity of functional groups was reached the nature of the reaction system changes from containing polymers with hydroxyl end-groups, V, into polymers with ureido end-groups, VI, as follows (where r = moles disilanol/moles bisureidosilane):



(4-6)

V(r>1.0) VI(r<1.0)

When all of the end-groups were of the ureido-type, any added quantity of bisureidosilane remained unreacted in the system. This excess of unreacted ureidosilane monomer could be easily and accurately observed by ^{1}H NMR spectroscopy. Final adjustments of the stoichiometric ratio were then performed by addition of the required quantity of arylenedisilanol until the absorptions due to unreacted bisureidosilane

disappeared. This method was adopted as the general method for preparation of poly(silarylene-siloxanes), and it proved to be capable of giving high molecular weight products ($\bar{M}_w$ > 250,000).

The characteristic absorptions in ^1H NMR spectra for the reaction mixtures are listed in Table 4-1. An illustration of this method of monitoring the condensation reaction is given in Figure 4-1.

2. Experimental

The preparation of polymer B from the p-diol and a mixture of dimethyl and methylvinyl ureidosilanes (containing 5 mole % of the latter) typifies the polymerization procedure as described before.

a. Materials

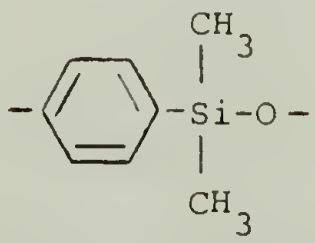
Bisureidosilane monomers were stored in closed 50 ml round-bottomed flasks filled with a dry nitrogen and kept in a desiccator under nitrogen, in the dark at -20°C. Disilanols were stored at room temperature and no special precautions were taken. Chlorobenzene was dried by refluxing twice for 12 hours each time over CaH_2, followed by distillation. The fraction with a sharp boiling point of 130°C was collected and stored over CaH_2 under nitrogen in a desiccator at room temperature.

b. Polymerization

A 100 ml, three-necked, round-bottomed flask was equipped with a Teflon-coated stirring bar, a dropping funnel with a serum cap and an inlet and outlet for an inert gas. The apparatus was assembled hot from the oven, flamed several times under vacuum and flashed with nitrogen.

TABLE 4-1

Assignments of the Characteristic ^{1}H NMR Peaks in the Spectra of Samples from the Polymerization Reaction Mixture

	Group	Chemical Shift (δ),[a] ppm	Type of Signal
Ureidosilane Monomer	$Si-CH_3$	0.98	singlet
	$-CH_2-N-CH_2-$	3.68	triplet
	$-CH_2-CH_2-$	1.80	quintet
Urea By-Product	$-CH_2-N-CH_2-$	3.90	triplet
	$-CH_2-CH_2-$	1.98	quintet
Polymer	$-O-Si(CH_3)_2-O-$	0.55	singlet
		0.80	singlet

[a]The internal standard was: methylenechloride; singlet at δ=5.30ppm

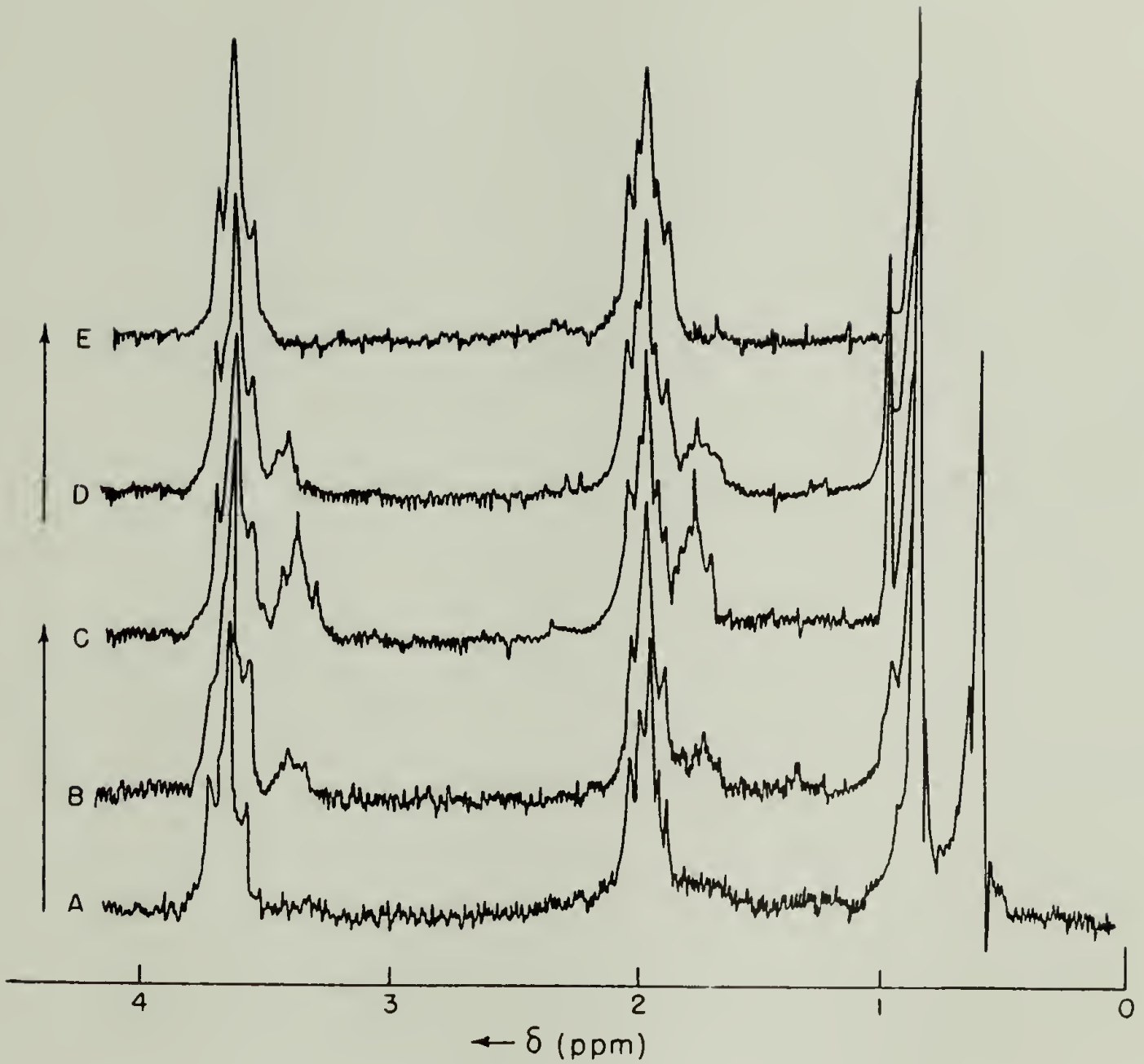


Figure 4-1. Monitoring the condensation polymerization by ^{1}H NMR spectroscopy: (A) original reaction mixture; (B) and (C) addition of ureidosilane; (D) and (E) addition of arylene disilanol.

Nitrogen was prepurified by passing it through series of columns containing H_2SO_4; KOH; P_2O_5 and molecular seaves ("Linde" type 3A, 1/16"). In a dry bag, 2.38g (10.51 mmole) of p-diol was placed into the reaction flask. A stock solution of the bisureidosilanes was prepared in another two-necked, 100 ml, round-bottomed flask equipped with a Teflon-coated stirring bar and a serum cap and maintained under a dry nitrogen atmosphere, which was dried as above. 5.58g (12.81 mmole) of dimethylureidosilane, III, and 1.50g (0.67 mmole) of methyvinylureidosilane, IV, were transferred into the flask in a dry bag and dissolved in 60.0 ml of chlorobenzene which had been transferred from a syringe. In such a way, 64.6 ml of a solution containing 13.48 mmole of the bisureidosilanes (c = 0.209 mmole/ml) was prepared.

The reaction flask containing solid p-diol was cooled down to -48°C dry-ice/acetone bath temperature. 43.0 ml of the stock solution containing 8.97 mmole of bisureidosilanes were transferred into the dropping funnel from a syringe and slowly added to the p-diol during 90 min under constant nitrogen flow. Stirring was started and during the addition the bath temperature was maintained between -48°C and -20°C. Molar ratio of two functionalities thus achieved was 1.175. Another 20 ml of chlorobenzene was added and the reaction mixture was allowed to warm up to room temperature during the next 3 hours. Three hours after the beginning of reaction another 1.6 ml of stock solution (containing 0.334 mmole of bisureidosilanes) was added during 30 min. The total amount of bisureidosilanes was thus increased to 9.30 mmole and the molar ratio decreased to 1.13. The ^1H NMR spectrum taken after

another two hours showed no presence of unreacted bisureidosilanes. Consequently, the stoichiometry was further adjusted with more of the same monomer until a molar ratio of 1.02 was reached and the first traces of unreacted bisureidosilanes were observed. The reactor was then transferred into a dry bag filled with nitrogen, and the stoichiometry was further adjusted with p-diol. After addition of 0.04g (0.175 mmole) all unreacted bisureidosilanes disappeared and final molar ratio equal to 1.04 was established after a total reaction time of 69 hours. Stirring was stopped and the reaction mixture was filtered through a sintered-glass funnel to separate polymer solution from urea by-product. The solution was then added dropwise into 800 ml of well-stirred methanol upon which a white, rubbery polymer precipitated. After decantation the polymer was dried for 54 hours at 25°C in a vacuum oven. 2.37g (78.4% yield relative to p-diol) of polymer was isolated. The polymer was an opaque, white, very viscous liquid. The urea by-product was dried for 30 hours at 50°C in a vacuum oven, upon which 3.18g (80.8% yield relative to bisureidosilanes) was isolated. A summary of this polymerization reaction is given in Table 4-2.

D. Monitoring of the Condensation Polymerization by Gel Permeation Chromatography (GPC)

To obtain high molecular weights in condensation polymerization the following requirements must be satisfied: (1) preparation of chemically pure (above 99%) monomers; (2) achievement of nearly quantitative conversions, p, ($p > 0.99$); and (3) establishment of equimolarity

TABLE 4-2

Preparation of Polymer B[a], p-diol Polymer with 5 Mole % Methylvinylsiloxane Units

Reaction Time, hours	p-diol, mmole	bisureidosilanes, mmole	$r=\frac{[\text{p-diol}]}{[\text{bisureidosilanes}]}$	Addition Time, min
0	10.54	8.97	1.18	90
3	10.54	+0.33 total=9.30	1.13	30
7.5	10.54	+0.50 total=9.80	1.08	60
25.5	10.54	+0.23 total=10.03	1.05	30
28.5	10.54	+0.12 total=10.15	1.04	15
45	10.54	+0.06 total=10.21	1.03	--
46	10.54	+0.13 total=10.34	1.02	30
56	+0.09 total=10.63		1.03	instant
68	+0.08 total=10.71		1.04	instant

[a]The reaction was started at -48 to -20°C but the temperature was increased to room temperature after 3 hours.

of the two different types of reactive functional groups ($r > 0.98$). If any of these three conditions is not satisfied high molecular weight polymers cannot be prepared by this route[2,3].

By applying these general considerations to the arylene-disilanol-bisureidosilane condensation system, the following conclusions could be drawn:

(1) According to the analytical techniques used for characterization of monomers, I-IV, it now appears that methods for their preparation have been perfected to give the products which satisfy the requirements imposed by the nature of a condensation polymerization reaction (Chapters II and III).

(2) ^{1}H NMR studies show that the basic reaction (Reaction 4-3) between the two functional groups is fast. This conclusion can be drawn from the known high reactivity of the ureido group towards nucleophilic substitution by the hydroxyl functional group, and it indicates that high conversions can be achieved. The data in Table 4-5 show that high yields of polymers were obtained in all syntheses, although all of these polymers are highly viscous liquids and very difficult to handle quantitatively. Because of this property at least 10-15% of the polymer is always lost during the course of its isolation from the reaction mixture and in the drying process. The yields reported in Table 4-5 are the yields of dry polymer, and because of the handling problems the amounts are undoubtedly lower than true yields achieved in the reaction.

(3) The third requirement for high molecular weight is the exact balance of the two reactive functional groups. As discussed in the previous section this can be routinely accomplished using ^{1}H NMR spectroscopy

to monitor the reaction. Nevertheless, as the goal is to achieve the highest possible molecular weights, the most direct method would of course be to directly follow the increase in this property as the molar ratio of two monomers approaches unity, rather than to follow another property which is only a function of the molecular weight, and then carry the reaction to the point where the molecular weight of the polymer ceases to increase any further. The obvious way to do that is to monitor the condensation polymerization by Gel Permeation Chromatography.

This method was evaluated during the course of the preparation of polymer J from a 50 mole % mixture of p-diol and ether-diol and a mixture of the two bisureidosilanes containing 5 mole % of the methyl-vinyl derivative. The reaction was performed in a usual way described before. About two hours after each addition of the bisureidosilane solution into the reaction mixture, a 0.5 ml sample of the liquid phase was removed and added to 10 ml of tetrahydrofuran. This solution was filtered, and 0.5 ml of the filtrate was injected into the chromatograph. Typical chromatogram is shown in Figure 4-2. It contains two peaks, a broader and smaller peak, A, at smaller elution volumes or shorter retention times, which is due to the polymer; and a sharper and more intensive peak, B, at larger elution volumes or longer retention times which is due to urea by-product and probably also to chlorobenzene solvent. As the polymerization reaction proceeded, the polymer peak shifted toward smaller elution volumes, while peak B remained at a constant position, and it could be used as an internal standard for monitoring the changes in the position of polymer peak.

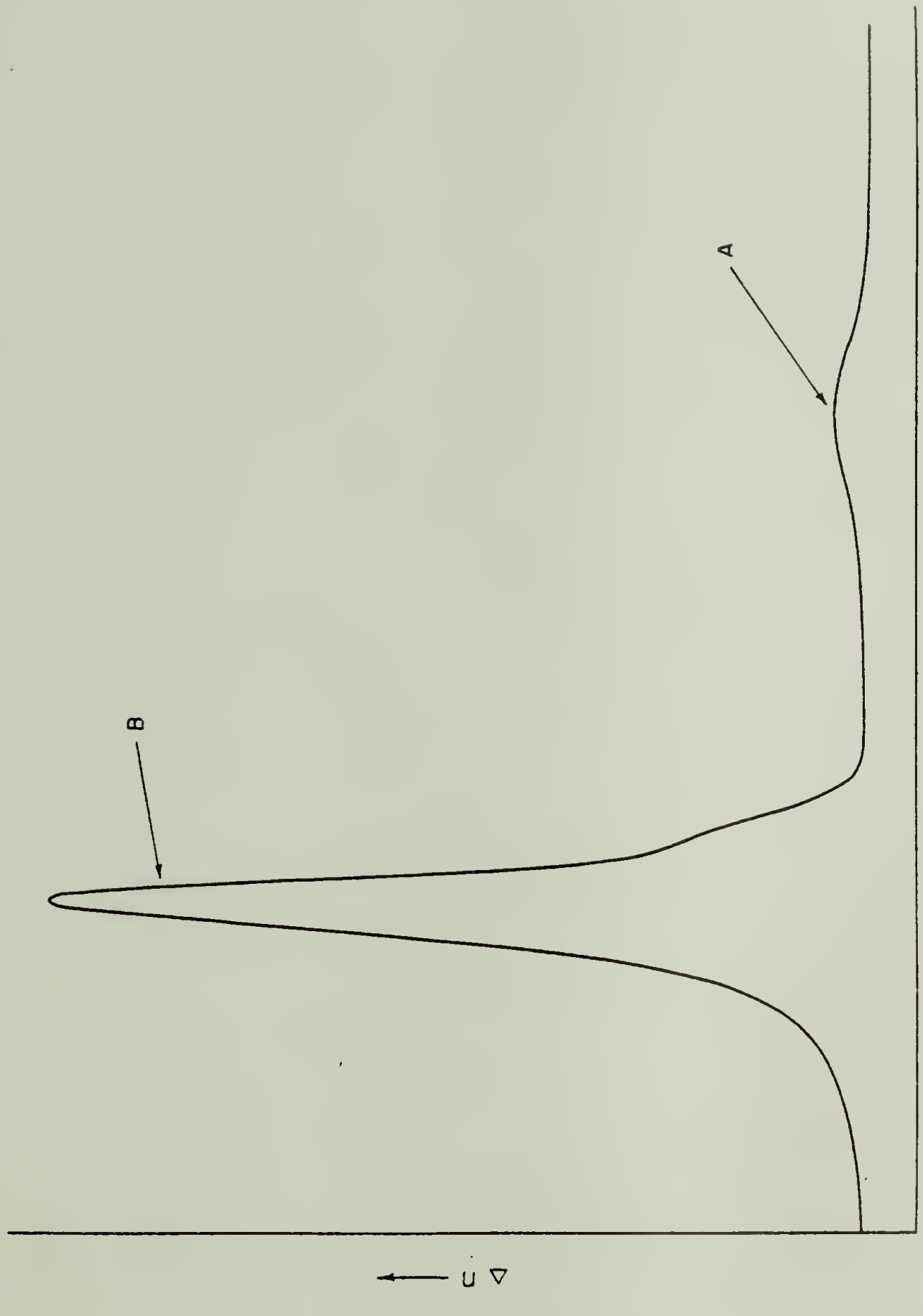


Figure 4-2. GPC Chromatogram of the condensation polymerization reaction mixture: (A) polymer; (B) urea by-product.

The following conclusions could be drawn from the use of this method when it was applied to the continuous monitoring of the condensation polymerization reaction as shown in Figure 4-3:

(1) During the most of the polymerization reaction (up to 1/r of 0.8), position of the polymer peak, A, shifted only slightly.

(2) Wehn 1/r reached 0.85-0.9 the position of A on the elution volume (or time) scale began to shift much more rapidly toward the smaller values.

(3) At very late stages in the reaction, when 1/r was greater than 0.99, the shifting of A slowed down and it completely ceased when the maximum molecular weight of the polymer was reached.

By use of a computer program[4] based upon a universal calibration curve for polystyrene standards, the molecular weights of the growing polymer at different values of r were calculated with the results presented in Table 4-3 and compared with values calculated on the basis of the equation below[2,3] in Figure 4-4:

$$\bar{M}_n = \bar{M}_0 \times \frac{1+r}{1-r} \qquad (4\text{-}7)$$

It could be seen from Figure 4-4 that the experimental behavior (curves A and B) followed that theoretically predicted (curve C). The experimental values were, however, somewhat larger than calculated. This could be understood on the basis of flexibility of the silarylene-siloxane chains; that is, they probably occupy larger hydrodynamic volumes than the stiffer polystyrene chains of the same length. Hence,

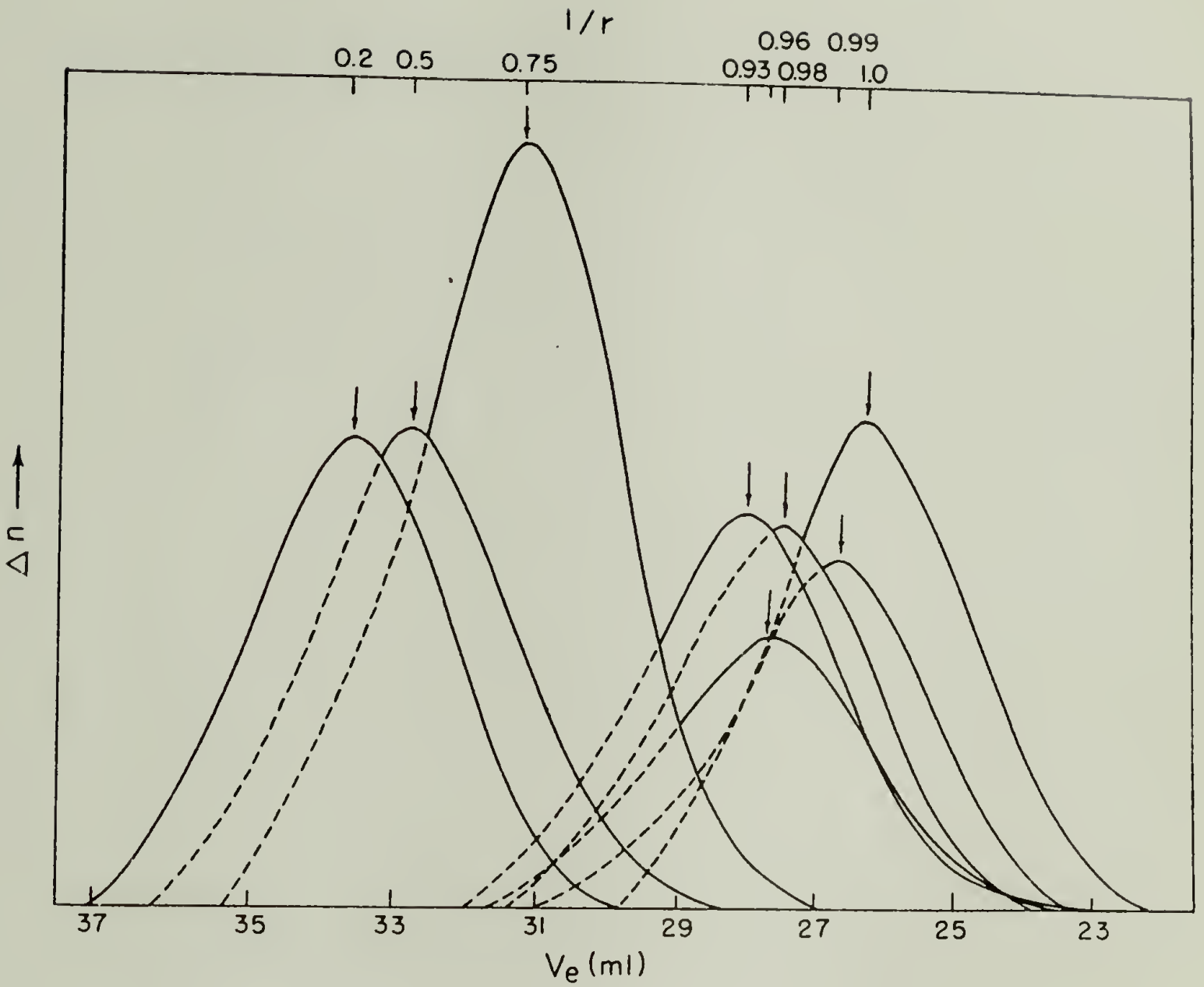


Figure 4-3. Monitoring of the condensation polymerization by GPC.

TABLE 4-3

Monitoring of the Condensation Polymerization by GPC

$\frac{1}{r} = \frac{[\text{bisureidosilane}]}{[\text{disilanol}]}$	$\overline{M_n}_{exp.}$	$\overline{M_w}_{exp.}$	$\overline{M_n} = \overline{M_o} \times \frac{1 + r}{1 - r}$
0.2	1000	2800	490
0.5	1250	5000	985
0.75	5200	13200	2300
0.935	46400	94800	9800
0.955	56600	108550	14300
0.98	57300	115900	32500
0.99	105950	170350	65400
final	118200	260000	-

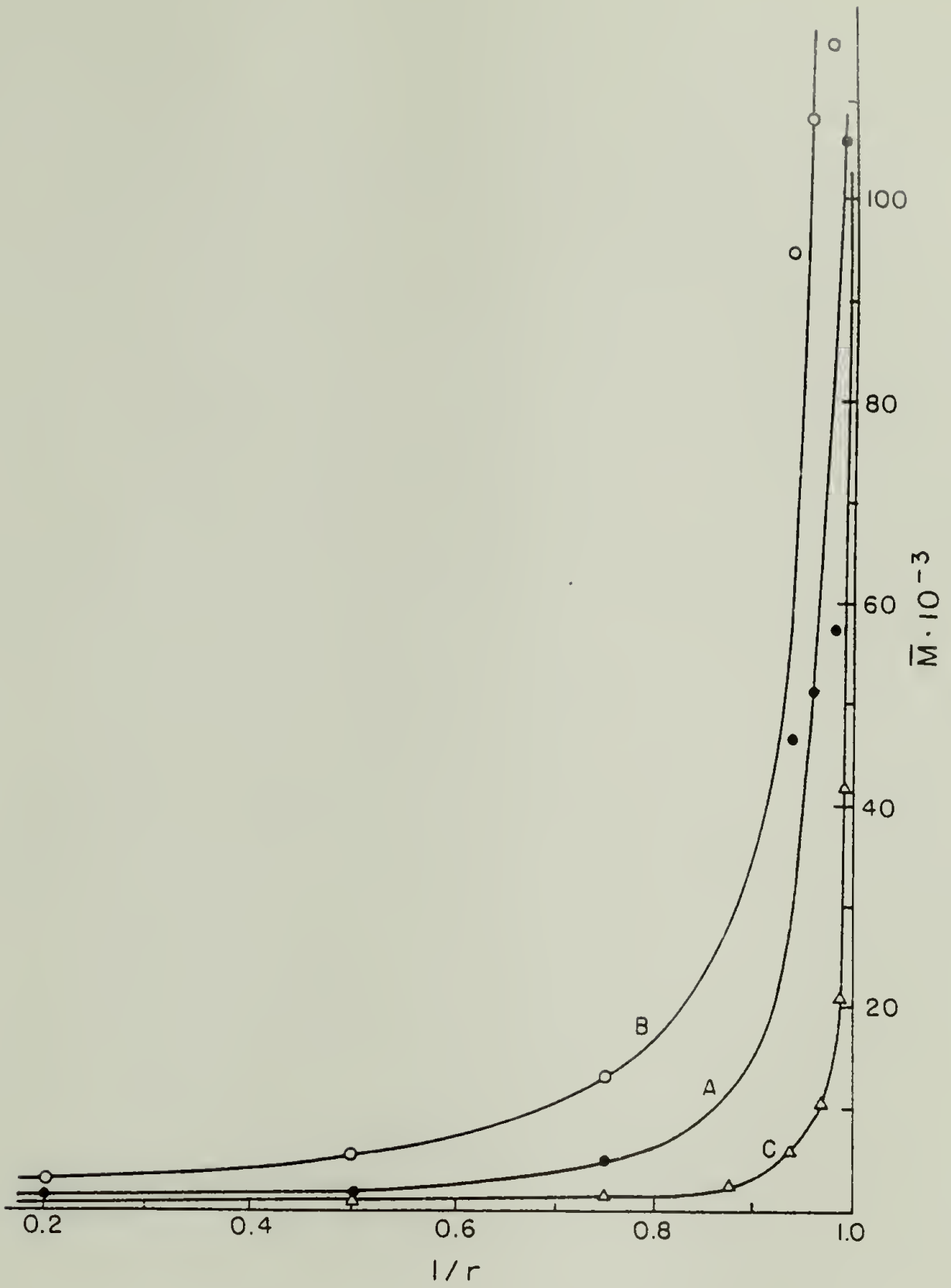


Figure 4-4. Increase in the molecular weight of growing polymer as a function of molar ratio of two monomers in the condensation polymerization reaction: (A) $\bar{M}_n$; (B) $\bar{M}_w$; (C) $\bar{M}_n$ (calcd.).

with all other conditions the same, retention times will be shorter for silarylene-siloxane polymers than for polystyrene of the equal molecular weight. This effect will then result in unrealistically high molecular weights for flexible chains and will shift the experimental curve upwards compared to the predicted one.

E. Conclusions

The condensation polymerization reaction of an arylenedisilanols with a bisureidosilanes (Reaction 4-2) was used to prepare a series of exactly alternating silarylene-siloxane polymers. Three groups of polymers were prepared as follows:

(1) polymers based upon the p-diol (I);

(2) polymers based upon the ether-diol (II); and

(3) polymers based upon a 50 mole % mixture of the two disilanols (0.5 I + 0.5 II).

Within each group the content of vinyl groups in the polymers was varied by varying the composition of the bisureidosilane mixture used so that the following samples were prepared:

(1) silarylene-dimethylsiloxane polymers based upon dimethylureidosilane (III);

(2) silarylene-methylvinylsiloxane polymers based upon methylvinylureidosilane (IV);

(3) polymers based upon 5 mole % and 7.5 mole % mixtures of methylvinyl and dimethylureidosilane (0.95 III + 0.05 IV and 0.925 III + 0.075 IV).

All the polymers prepared are tabulated in Table 4-4 and a summary of the synthetic parameters for all of the polymerization reactions is presented in Table 4-5.

The following conclusions could be drawn from the results discussed in this chapter:

(1) The condensation polymerization of arylenedisilanols and bisureidosilanes, under the conditions described, gave yields of at least 95% of the polymers. However, not all of the polymers could be isolated in so high yields because on average 10-15% of the product was usually lost in handling and drying because of its high viscosity.

(2) The urea by-product was much easier to isolate, and practically quantitative yields were obtained.

(3) ^{1}H NMR spectroscopy showed that the reaction was very rapid which enabled the use of low reaction temperatures and variations in the conditions employed.

(4) Apparently even at low reaction temperatures there was still some ether-type disilanol condensation occurring (Reaction 4-4) which manifested itself in the final molar ratio r of two required monomers which was always a few per cent higher than unity. However, if it was never more than 4% (Table 4-5) it would probably not influence polymer properties to any large extent.

(5) The high reactivity of the bisureidosilanes enabled the use of a wide variety of modifications of the polymer backbone, as was done here as well as in the work of previous authors on different polymers[1].

TABLE 4-4

Exactly Alternating Silarylene-Siloxane Polymers

GROUP I

(based upon p-diol monomer)

polymer A	I + III
polymer B	I + (0.95 III + 0.05 IV)
polymer C	I + (0.925 III + 0.075 IV)
polymer D	I + IV

GROUP II

(based upon ether-diol monomer)

polymer E	II + III
polymer F	II + (0.95 III + 0.05 IV)
polymer G	II + (0.925 III + 0.075 IV)
polymer H	II + IV

GROUP I + II

(based upon 50 mole % mixture of the two disilanols)

polymer I	(0.5 I + 0.5 II) + III
polymer J	(0.5 I + 0.5 II) + (0.95 III + 0.05 IV)
polymer K	(0.5 I + 0.5 II) + (0.925 III + 0.075 IV)
polymer L	(0.5 I + 0.5 II) + IV

TABLE 4-5

Synthetic Parameters in Preparation of Polymers from Table 4-4

Disilanol	% vinyl	Polymer	Disilanol mmole	Bisureidosilanes mmole	Final Value of r	Total Reaction Time, hours	Polymer Yield, %	Urea Yield, %	Average r for the group
E-diol (I)	0	A	30.696	29.572	1.038	352	94.38	99.43	1.035
	5	B	10.716	10.347	1.036	96	78.37	80.84	
	7.5	C	19.243	18.670	1.032	69	85.47	90.18	
	100	D	17.640	19.798	0.891*	130	86.70	96.71	
ether-diol (II)	0	E	16.737	16.490	1.015	405	89.87	88.56	1.012
	5	F	17.340	17.578	0.986*	72	78.87	91.97	
	7.5	G	17.699	17.403	1.017	74	78.85	82.29	
	100	H	16.720	16.337	1.005	47	82.46	97.93	
50 mole % mixture of two disilanols (0.5I+0.5II)	0	I	20.498	19.940	1.028	48	93.17	97.32	1.025
	5	J	20.085	19.892	1.010	99	85.93	90.24	
	7.5	K	20.299	19.787	1.026	52	69.35	95.84	
	100	L	20.385	19.696	1.035	51	80.12	89.50	

*disregarded when $r_{average}$ was calculated.

(6) A successful monitoring of the condensation polymerization reaction proves to be of crucial importance for preparation of high molecular weight polymers. It is interesting to note that the use of GPC for monitoring purposes provided a final molar ratio of two monomers much closer to 1.00 (Polymer J in Table 4-5) than did ^{1}H NMR spectroscopy (Polymers I, K and L in the same Table 4-5) what resulted in significantly higher molecular weight of the Polymer J as compared with the other three polymers in the following chapter. This result may indicate that the sensitivity of ^{1}H NMR spectroscopy was inferior for these purposes to the sensitivity of GPC.

(7) In all cases, except in the case of Polymer F, high molecular weight products (see Chapter V) were obtained and polymers with $\bar{M}_w$ above 200,000 could be routinely prepared.

(8) Elemental analyses of all polymers [7] were performed by the Microanalytical Laboratory of the University of Massachusetts. The results obtained are presented in Table 4-6 and compared with the values calculated on the basis of the predicted structures of repeating units. The results obtained in all cases were in satisfactory agreement with the calculated values.

TABLE 4-6

Elemental Compositions of Alternating Silarylene-Siloxane Polymers

Polymer	Disilanol	% vinyl	% C		% Si		% H		% O	
			calc.	found	calc.	found	calc.	found	calc.	found[a)]
A	p-diol	0	51.06	50.18	29.79	29.98	7.80	8.36	11.35	11.48
B		5	51.18	47.88	29.78	30.58	7.78	7.81	11.32	12.11
C		7.5	51.22	50.41	29.69	29.51	7.78	7.97	11.31	12.11
D		100	53.06	51.97	28.57	28.67	7.48	7.26	10.88	12.10
E	ether-diol	0	57.75	56.04	22.46	23.14	6.95	6.76	12.84	14.06
F		5	57.82	54.30	22.42	23.89	6.94	7.22	12.81	14.59
G		7.5	57.84	57.64	22.40	22.89	6.93	7.01	12.80	12.46
H		100	59.07	59.43	21.76	21.70	6.74	6.66	12.43	12.21
I	50 mole % mixture	0	54.88	54.93	25.61	25.30	7.32	7.58	12.19	12.19
J		5	54.96	53.80	25.56	25.76	7.30	7.54	12.17	12.90
K		7.5	55.00	54.18	25.54	25.57	7.30	7.46	12.16	12.79
L		100	56.47	56.01	24.71	24.37	7.06	7.15	11.76	12.47

a) $\%\ O_{found} = 100 - (\%\ C + \%\ Si + \%\ H)_{found}$

Bibliography

1. E. Hedaya, J.H. Kawakami, P.W. Kopf, G.T. Kwiatkowski, D.M. McNeil, D.A. Owen, E.N. Peters, "D_2-meta Carborane-Siloxanes. IV. Synthesis of Linear, High Molecular Weight Polymers", J. Polymer Sci., Polymer Chem. Ed., 15, 2229 (1977).
2. R.W. Lenz, "Organic Chemistry of Synthetic High Polymers", Interscience, New York (1967); p. 53 ff.
3. G. Odean, "Principles of Polymerization", McGraw-Hill, New York (1970); p. 40 ff.
4. E.M. McCaffery, "Laboratory Preparation for Macromolecular Chemistry", McGraw-Hill, New York (1970); p. 368.
5. W.R. Sorenson, T.W. Campbell, "Preparative Methods of Polymer Chemistry", Interscience, New York (1968); p. 187.
6. L.W. Breed, R.L. Elliott, M.E. Whitehead, "Arylene-Modified Siloxanes", J. Polymer Sci., A-1, 5, 2745 (1967).
7. G.J. Shugar, R.A. Shugar, L. Bauman, "Chemical Technician's Ready Reference Handbook", McGraw-Hill, New York (1973); p. 245.

C H A P T E R V

PHYSICAL CHARACTERIZATION OF EXACTLY ALTERNATING SILARYLENE-SILOXANE POLYMERS

A. Introduction

In order to characterize the silarylene-siloxane polymers extensive structural analyses by a number of different methods was performed. These investigations included: ^{1}H NMR spectroscopy, IR spectroscopy, ^{13}C NMR spectroscopy, gel permeation chromatography (GPC), dilute solution viscometry and differential scanning calorimetry (DSC). This chapter describes the techniques and the interpretation of structural information obtained.

B. ^{1}H NMR Spectroscopy

The spectra of silarylene-siloxane homopolymers and copolymers(*) were recorded using a Perkin Elmer 90 MHz Spectrometer (Model R-32). Deuterated chloroform was used as solvent at 30°C, and methylene chloride was used as reference and internal lock substance (singlet at

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(*) The term "copolymer" is used here to refer to the polymers prepared from the mixtures of two bisureidosilanes while "homopolymer" denotes the polymers prepared from a single bisureidosilane monomer.

δ = 5.30 ppm relative to tetramethylsilane). Chemical shifts of characteristic absorption peaks and their assignments are presented in Table 5-1, and the spectra are shown in Figures 5-1 and 5-5.

The following general conclusions could be drawn from these spectra:

(1) All twelve polymers showed very sharp spectra regardless of their high molecular weights (see Sections E and F of this chapter). This result is unusual for high polymers, which tend to show broad and somewhat distorted peaks[1]. The sharpness of the peaks in the spectra of alternating silarylene-siloxanes most probably resulted from their high solubility and the pronounced flexibility of the chains.

(2) All twelve polymers showed characteristic absorption singlets at δ = 0.10 ppm and δ = 0.35 ppm[**] which originated from the protons of the methyl groups attached to the silicon in (-O-Si-O-) and (-Ar-Si-O-) units, respectively. In all three groups of polymers the ratio of the integrals of 0.35 ppm and 0.10 ppm peaks was equal to two for all-methyl polymers, prepared from dimethylureidosilane (Polymers A, E and I) while the same ratio became four in the case of the all-vinyl polymers prepared from methylvinylureidosilane (Polymers D, H and L). These ratios are considered to be the strongest evidence for exactly alternating structures.

(3) The 0.10 ppm peak did not shift or change its shape with increasing pendant vinyl group content in the polymers, indicating that there were no significant coupling effects between the protons from vinyl and methyl groups attached to the same silicon atom.

[**] All ^{1}H NMR chemical shifts are relative to tetramethylsilane.

TABLE 5-1

Characteristic Absorptions and Peak Assignments in ^1H NMR Spectra of Alternating Silarylene-Siloxane Polymers

Polymer	$-OSi(CH_3)_2O-$ (singlet)	$-OSi(CH_3)_2Ar-$ (singlet)	$-C_6H_4-$ (singlet)	$-C_6H_4-O-C_6H_4-$ (two doublets)		$-CH=CH_2$ (quartet)
A	0.10	0.35	7.60			
B	0.10	0.35	7.60			5.90
C	0.10	0.40	7.65			5.90
D	0.10	0.35	7.60			5.95
E	0.10	0.35		7.05	7.55	
F	0.10	0.30		7.05	7.55	
G	0.10	0.35		7.05	7.55	6.30
H	0.10	0.35		7.05	7.55	5.95
I	0.10	0.35	7.60	7.05	7.55	
J	0.10	0.35	7.60	7.05	7.55	
K	0.10	0.35	7.60	7.05	7.55	5.95
L	0.10	0.35	7.60	7.05	7.55	5.95

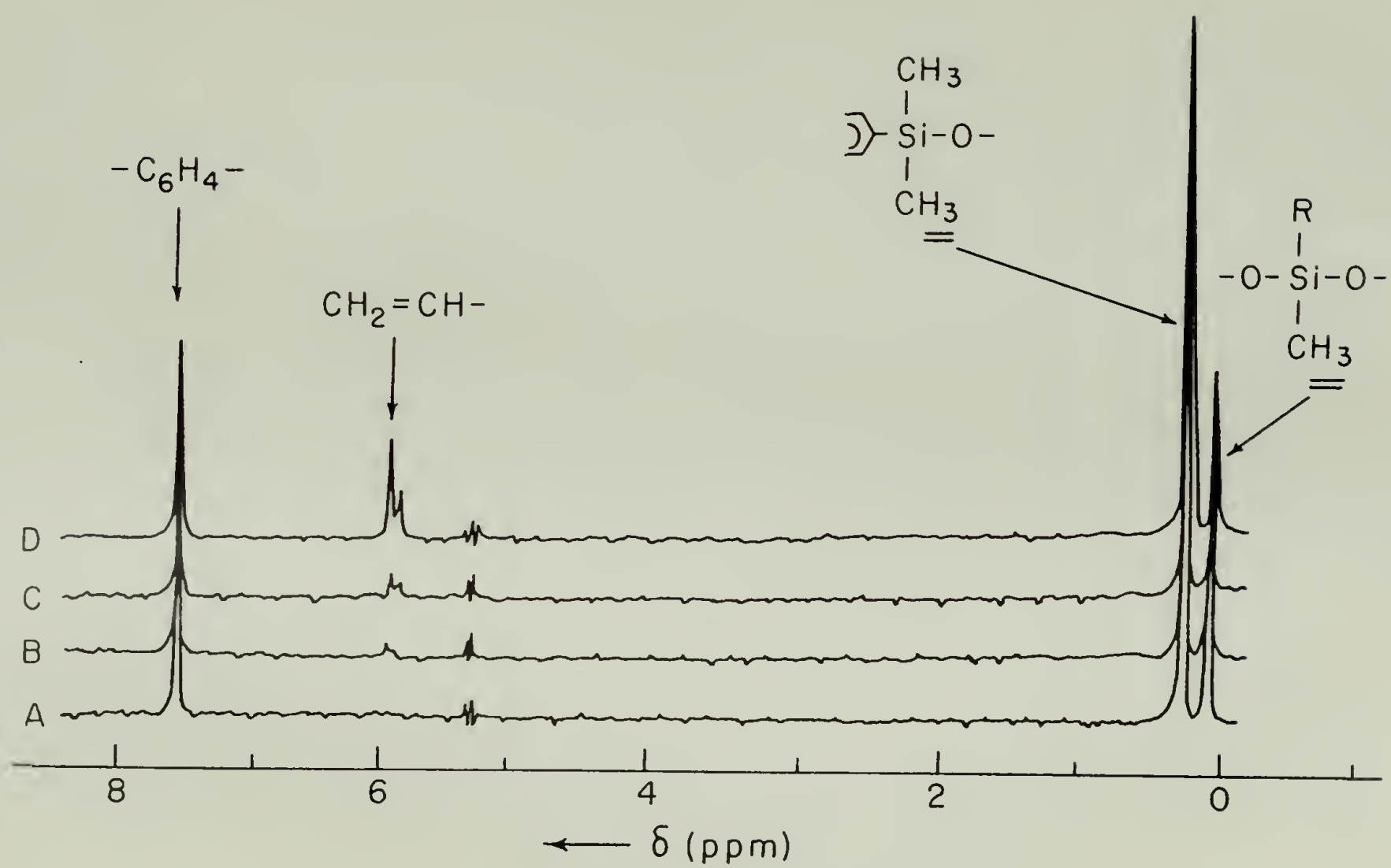


Figure 5-1: ^1H NMR spectra of the polymers prepared from the p-diol monomer.

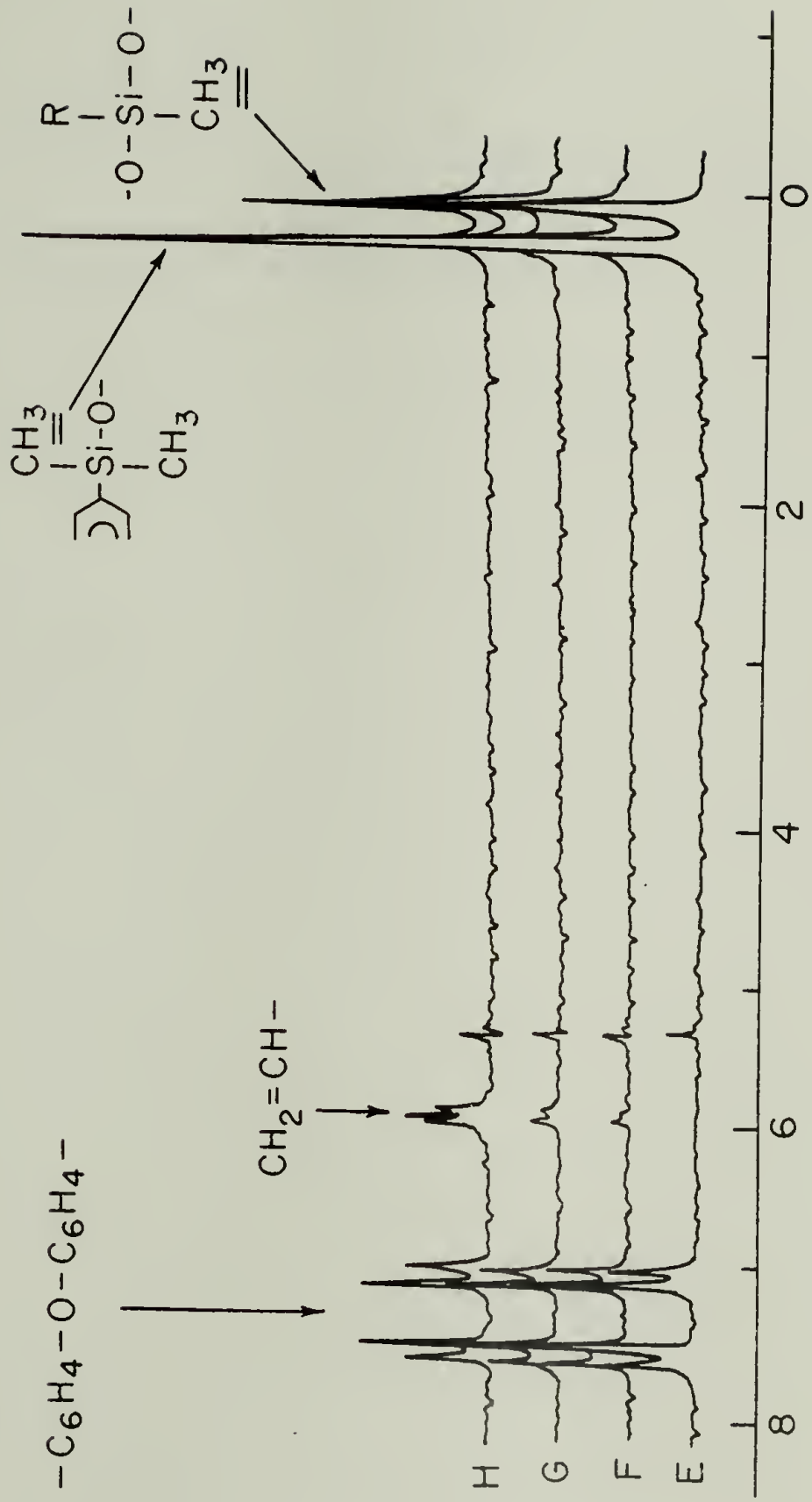


Figure 5-2. ^{1}H NMR spectra of the polymers prepared from the ether-diol monomer.

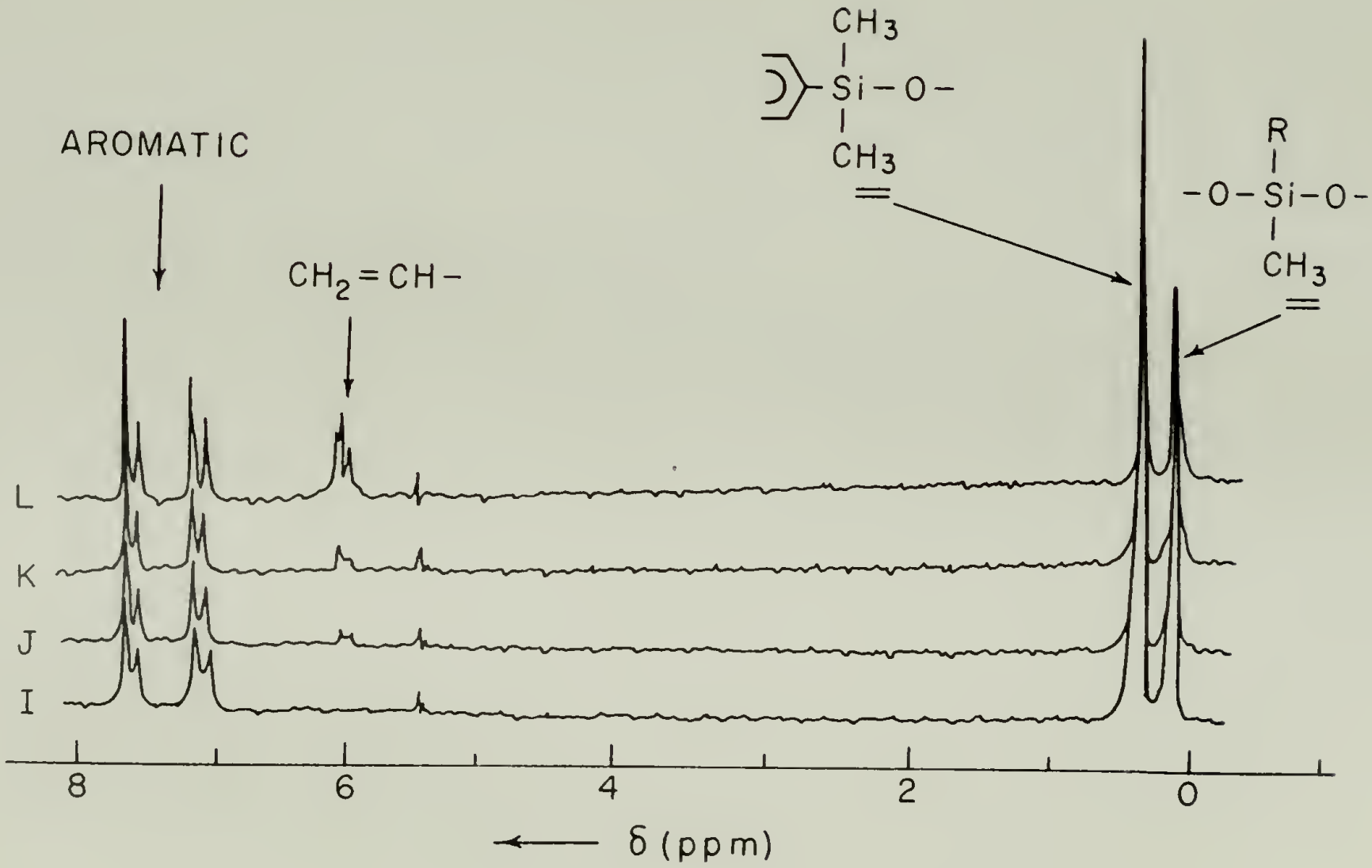


Figure 5-3. ^1H NMR spectra of the polymers prepared from a 50 mole % mixture of the two arylenedisilanols.

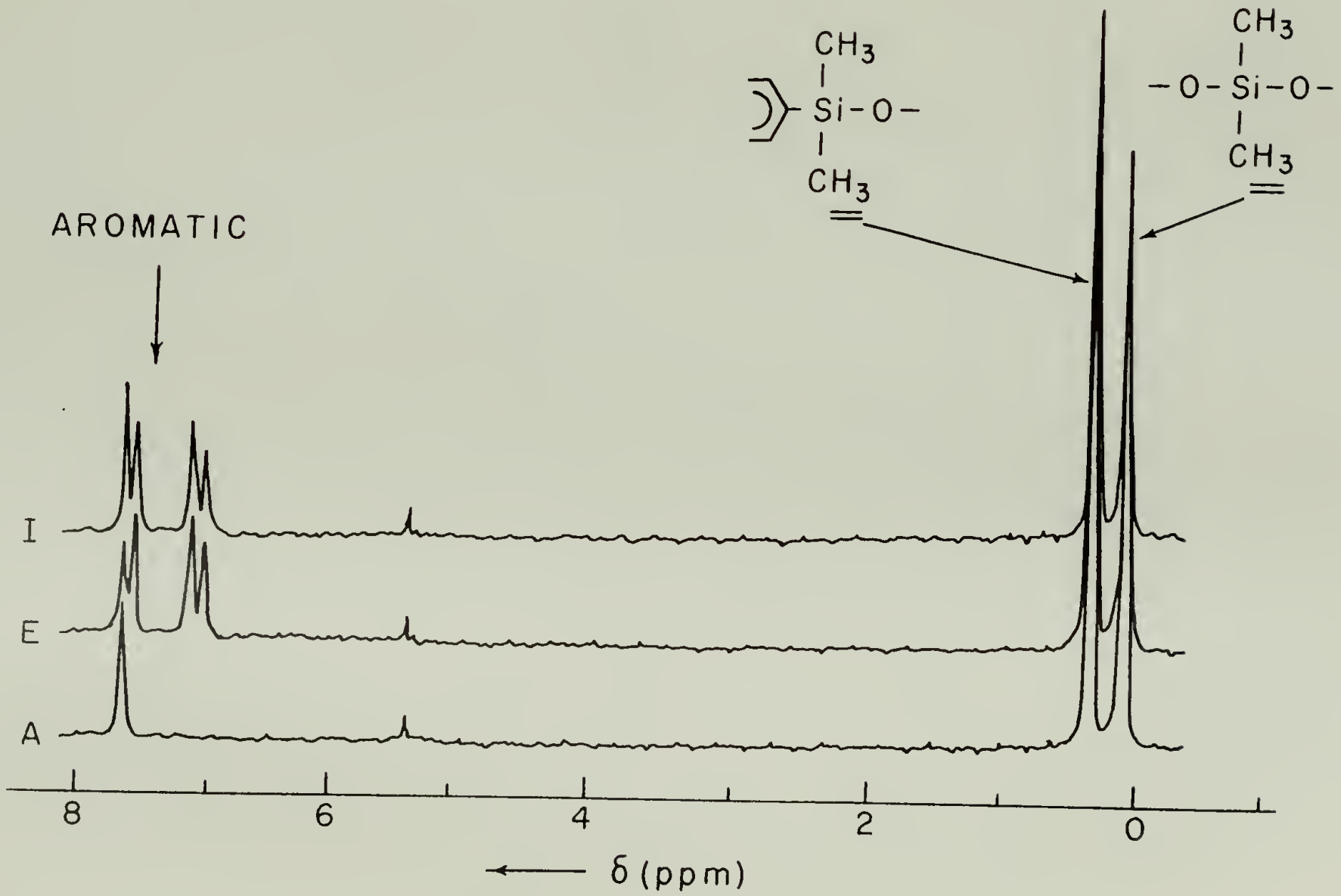


Figure 5-4. ^{1}H NMR spectra of the polymers prepared from dimethylureidosilane.

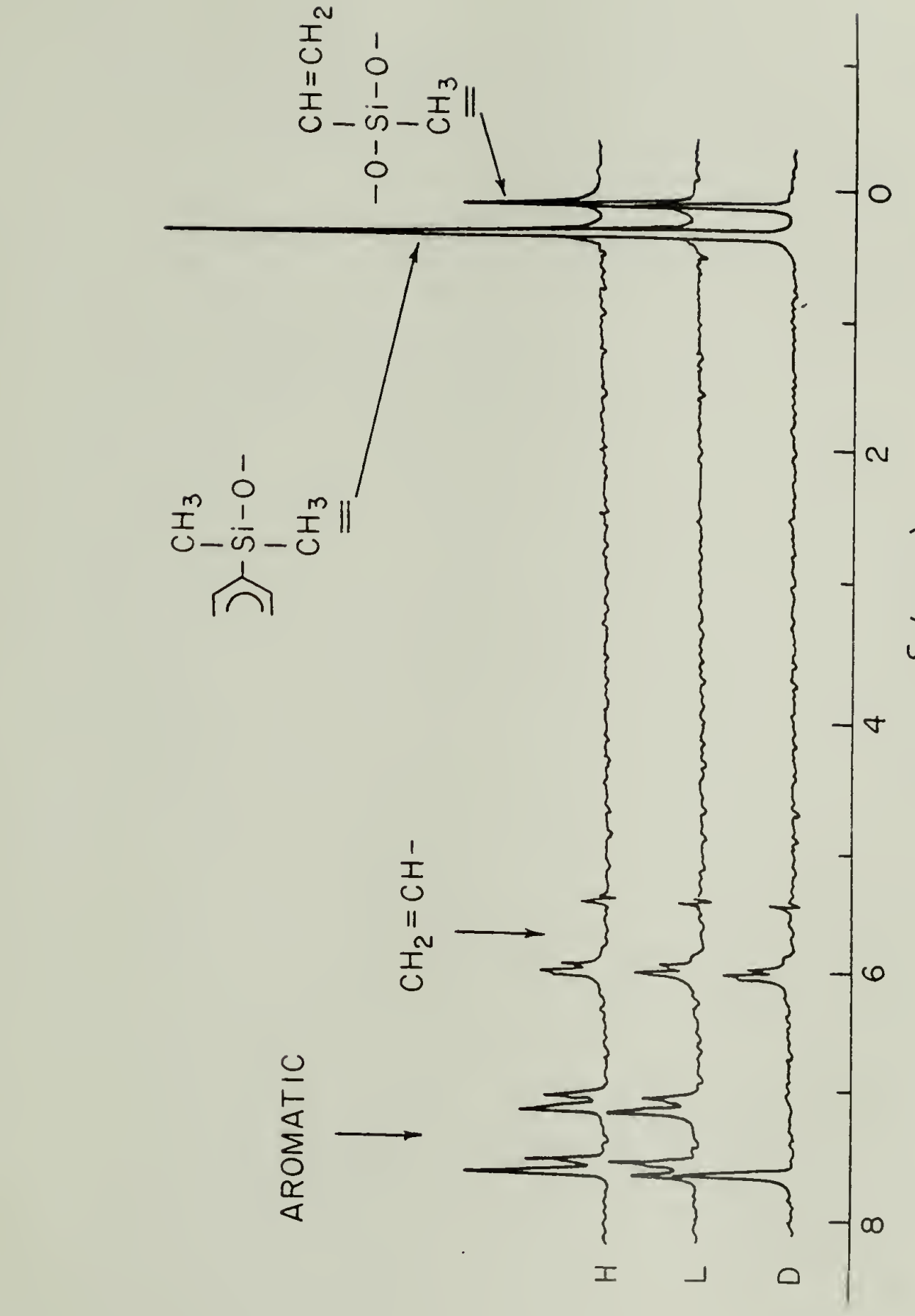
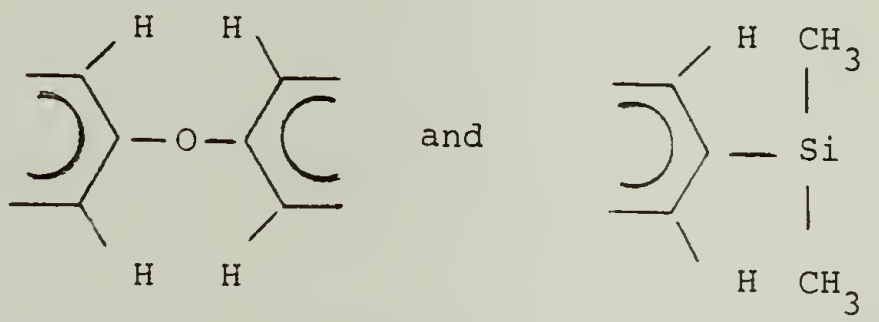


Figure 5-5. ^{1}H NMR spectra of the polymers prepared from methylvinylureidosilane.

(4) All the polymers prepared from the p-diol monomer (Polymers A, B, C and D) showed sharp singlet at δ = 7.60 ppm as would be expected for four equivalent aromatic protons in a $-C_6H_4-$group.

(5) All the polymers prepared from the ether-diol monomer (Polymers E, F, G and H) showed two sharp doublets at δ = 7.05 ppm and δ = 7.55 ppm with J = 8 cps in both cases. These peaks were due to the presence of two types of nonequivalent protons in the aromatic diphenyl ether group and could be assigned to the following structures, respectively:



(6) The absorption peak of the protons from a $-C_6H_4-$group overlapped with the peak of the 7.55 ppm doublet in the ether-diol polymers to create a characteristic distorted doublet in case of the polymers prepared from the 50 mole % mixture of the two arylenedisilanols (Figure 5-3).

(7) Vinyl group protons showed characteristic quartets at δ = 5.95 ppm. This quartet was of unexpectedly strong intensity and could be easily observed even in the case of polymers in which only 5 mole % of all of the ~~(O-Si-O)~~ segments had vinyl groups. It is interesting to note here that such was not the case with ^{13}C NMR spectroscopy where it was not possible to observe absorption due to vinyl group carbons even at the 7.5 mole % level (Section 5-D).

C. Infrared Spectroscopy

Infrared spectra of all twelve alternating silarylene-siloxane polymers were recorded on a Perkin Elmer Infrared Spectrophotometer (Model 283). The samples were cast film from 5% ($^{w}/v$) polymer solutions in tetrahydrofuran. Casting was done directly on the sodium chloride plates, and after the evaporation of the solvent, the films were dried at 25°C for approximately six hours. All the spectra were recorded within the wavenumber range of 4000 to 600 cm^{-1} at 25°C. Characteristic absorptions are listed in Tables 5-2 to 5-4 and the spectra are presented in the Appendix I.

The following general conclusions and observations could be drawn from the infrared data:

(1) Infrared spectroscopy was only useful for qualitative analysis of the polymers, and the characteristic absorptions of the functional groups could be observed and assigned[2,3,9].

(2) The infrared method did not seem to be very useful for quantitative analysis, particularly for vinyl group determination. The absorption peaks for these groups were characteristically weak and in some cases when vinyl content was low, peaks could not be seen (Polymers J, F: absorption at 940-960 cm^{-1}).

(3) Alternating silarylene-siloxane polymers could be cast into films from tetrahydrofuran solution. The films were clear and transparent, but they adhered tightly to the sodium chloride surface and could not

TABLE 5-2

Infrared Assignments for Alternating Silarylene-Siloxane Polymers Prepared from the p-diol Monomer

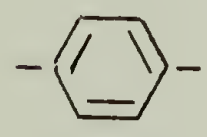
Assignments	Polymer Samples			
	A	B	C	D
C-H stretching (CH_3)	2900-3080 2960	2900-3080 2960	2900-3080 2960	2900-3080 2960
	1395 1410	1390 1410	1385 1410	1380 1405
Si-CH_3	1310 1240-1260	1310 1240-1260	1310 1240-1260	-- 1240-1260
Si-C	870 825 790	- 820 790	860 825 785	- 820 780
-O-Si-O-	1115 1040	1115 1045	1115 1050	1115 1040
 -Si	1175	1160	1140	1140
CH_2=CH-	--	940	960	960

TABLE 5-3

Infrared Assisgnments for Alternating Silarylene-Siloxane Polymers Prepared from the Ether-diol Monomer

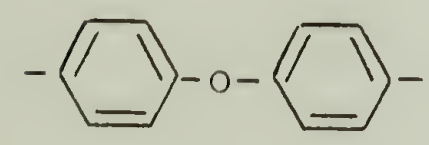
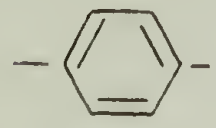
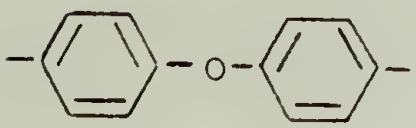
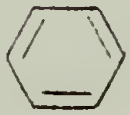
Assignments	Polymer Samples			
	E	F	G	H
C-H stretching (CH_3)	2900-3080 2960	2900-3080 2960	2900-2080 2960	2900-3080 2960
	1585	1585	1585	1585
	1395 1410	1395 1410	1395 1410	1390 1410
Si-CH_3	1310 1240-1260	1310 1240-1260	1305 1240-1260	1310 1240-1260
Si-C	860 825	865 825	870 825	870 825
 -Si	790 1175	780 1175	780 1175	780 1175
O-Si-O	1115 1040	1115 1040	1115 1040	1115 1040
CH_2=CH-	-- --	-- 1730	940 1730	960 1730

TABLE 5-4

Infrared Assignments for Alternating Silarylene-Siloxane Polymers from a 50 mole % Mixture of the Two Arylenedisilanols

Assignments	Polymer Samples			
	I	J	K	L
C-H stretching (CH_3)	2900-3080 2960	2900-3080 2960	2900-3080 2960	2900-3080 2960
	1585	1585	1585	1585
	1380 1410	1380 1405	1365 1410	-- 1410
$Si-CH_3$	1310 1240-1260	1310 1240-1260	1310 1240-1260	-- 1240-1260
Si-C	870 825 790	870 825 790	870 825 780	870 825 775
 -Si	1175	1175	1175	1175
O-Si-O	1115 1040	1115 1040	1115 1040	1115 1040
Ch_2=CH-	-- --	-- 1730	940 1730	960 1730

be peeled off for further use without breaking.

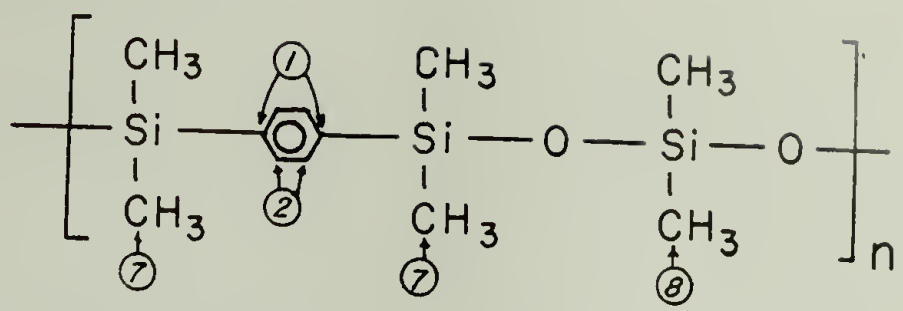
(4) Some preliminary results indicated that IR analysis might be a useful method for the determination of the crystallinity in these and similar polymers, if such existed[4]. However, detailed studies in this area are needed in order to draw definite conclusions (see Section G of this chapter).

D. ^{13}C NMR Spectroscopy

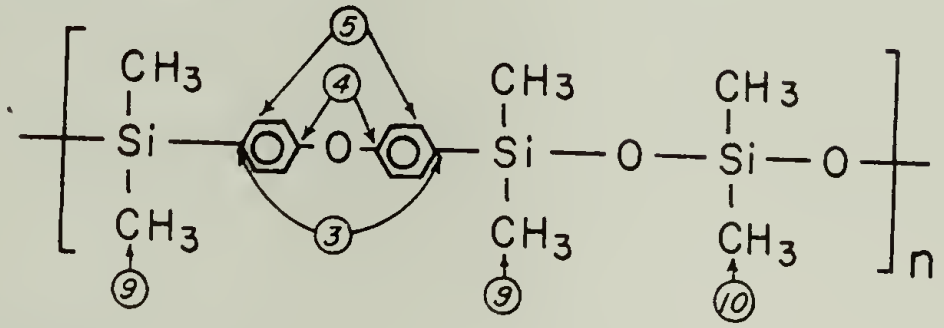
The spectra of silarylene-siloxane polymers were recorded using a Varian CFT-20 ^{13}C NMR Spectrometer. Deuterated chloroform was used as the solvent and reference substance (triplet at δ = 76.91 ppm relative to tetramethylsilane). Sample concentrations ranged from 0.2 to 0.3g of polymer per 2 ml of solvent. Spectral range of 180 ppm was covered in all cases and about 10,000 acquisitions were usually enough for an acceptable signal to noise ratio. An acquisition time of 1.023 sec per pulse was used with 2.0 sec delays between pulses. The other common operating parameters were: spectral width: 4000 Hz, pulse width: 15 µsec, data points: 8184, noise bandwidth: 1000 Hz, sensitivity enhancement: -0.200 sec, spin rate: 20 rps and temperature: 40°C.

Chemical shifts relative to tetramethylsilane of characteristic absorption peaks and their assignments are presented in Table 5-5 and the spectra are shown in Figures 5-7 to 5-11. Figure 5-6 explains the numbering system used to identify the different carbon atoms. Table 5-6 compares observed chemical shifts and the values calculated on the basis

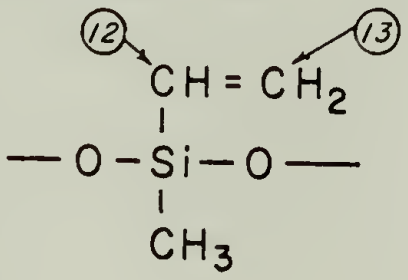
p-diol Polymers:



Ether-diol Polymers:



Vinyl Carbons (v):



Polymers from a 50 mole % Mixture of the 2 Disilanols:

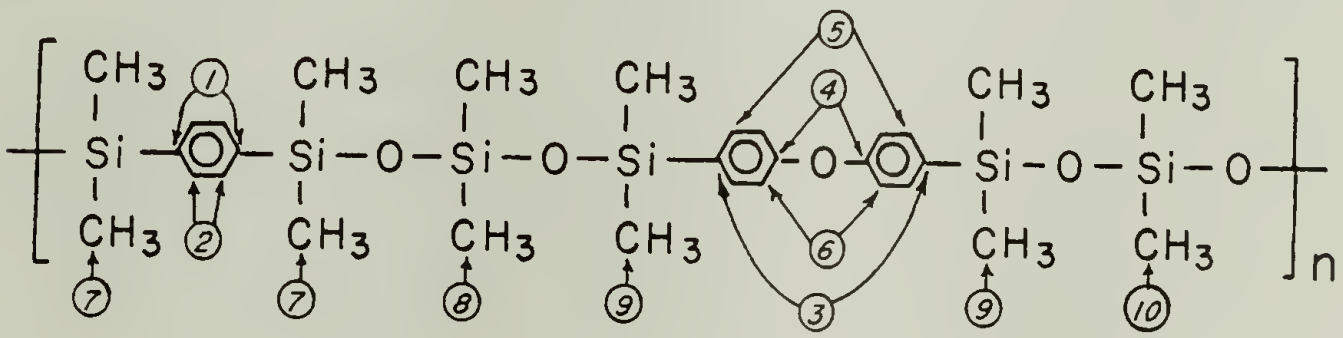


Figure 5-6. Numbering of the carbon atoms in ^{13}C NMR spectra of alternating silarylene-siloxane polymers.

TABLE 5-5

Characteristic Absorptions and Peak Assignments in ^{13}C NMR Spectra of Alternating Silarylene-Siloxane Polymers

Polymers from p-diol monomer		Polymers from ether-diol monomer		Polymers from 50 mole % mixture of diols	
δ(ppm)	assignment	δ(ppm)	assignment	δ(ppm)	assignment
		158.02	C_4	158.01	C_4
140.58	C_1			140.70	C_1
137.15	C_{12}	137.13	C_{12}	137.14	C_{12}
		134.62	C_6	134.62	C_6
		134.09	C_3	134.12	C_3
132.88	C_{13}	132.89	C_{13}	132.90	C_{13}
132.15	C_2			132.13	C_2
		118.16	C_5	118.20	C_5
		1.26	C_{10}	1.26	C_{10}
1.25	C_8			1.15	C_8
		0.75	C_9	0.74	C_9
0.68	C_7			0.66	C_7
-0.60	C_{11}	-0.57	C_{11}	-0.52	C_{11}

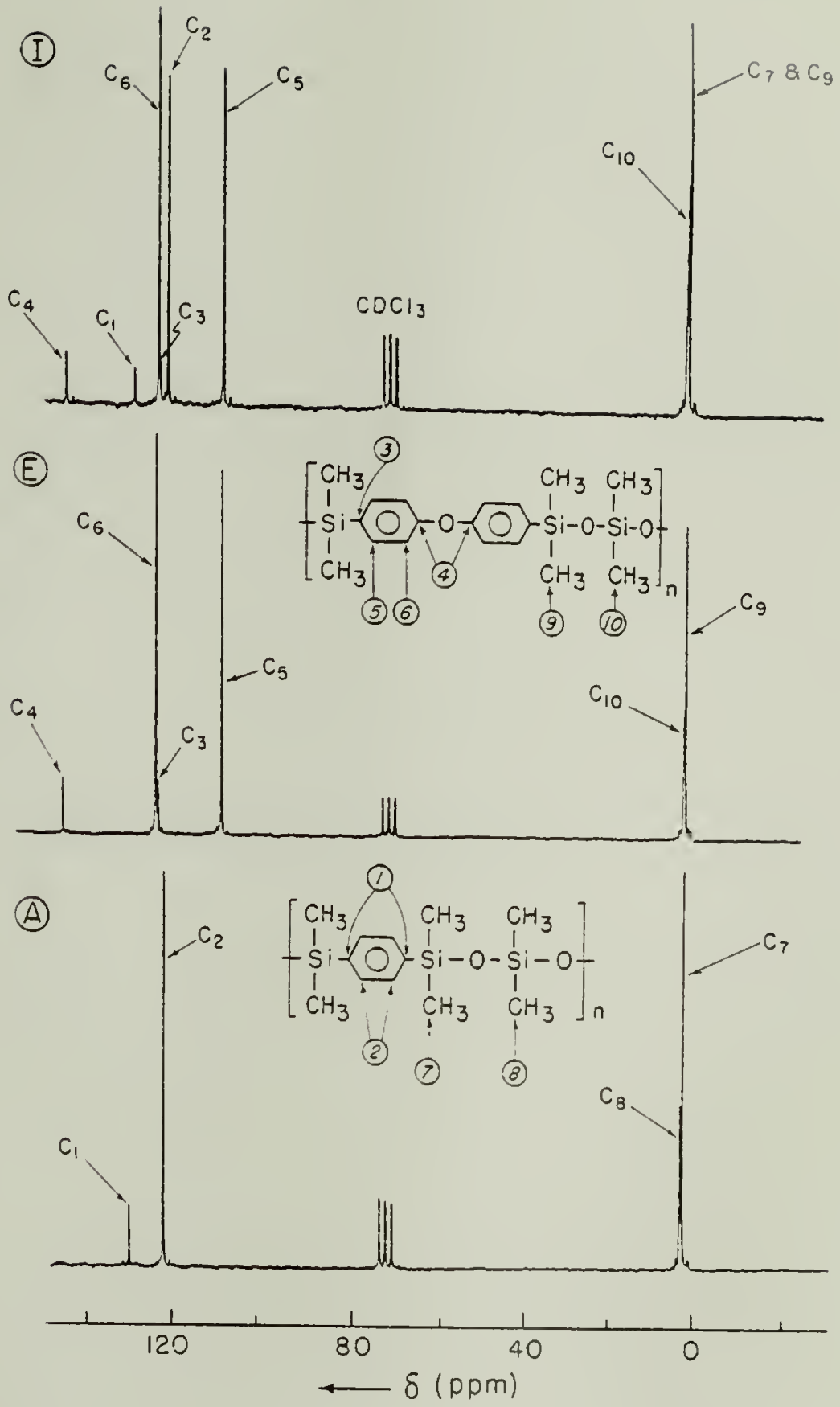


Figure 5-7. ^{13}C NMR spectra of the polymers prepared from dimethylureidosilane.

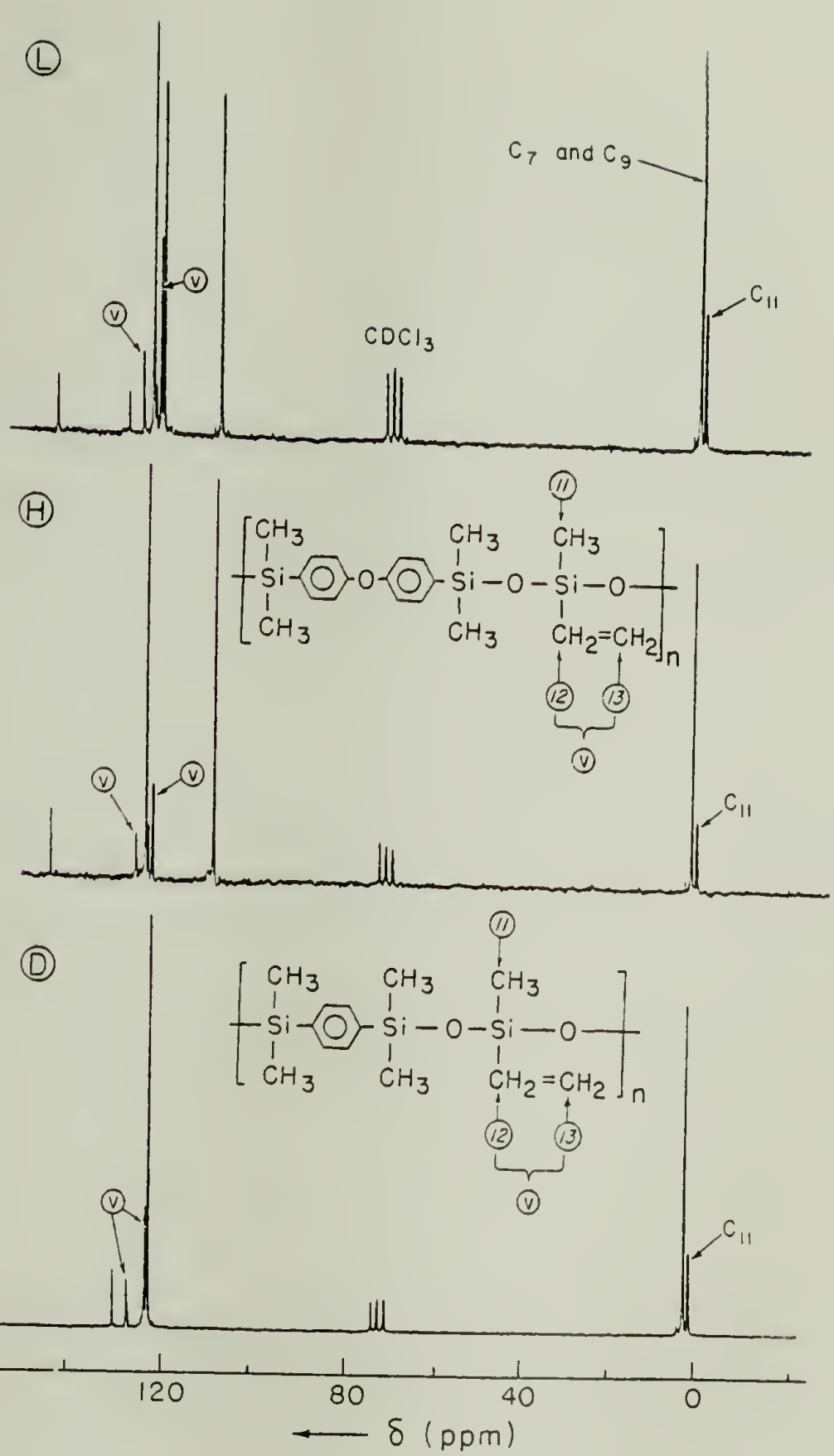


Figure 5-8. ^{13}C NMR spectra of the polymers prepared from methylvinylureidosilane.

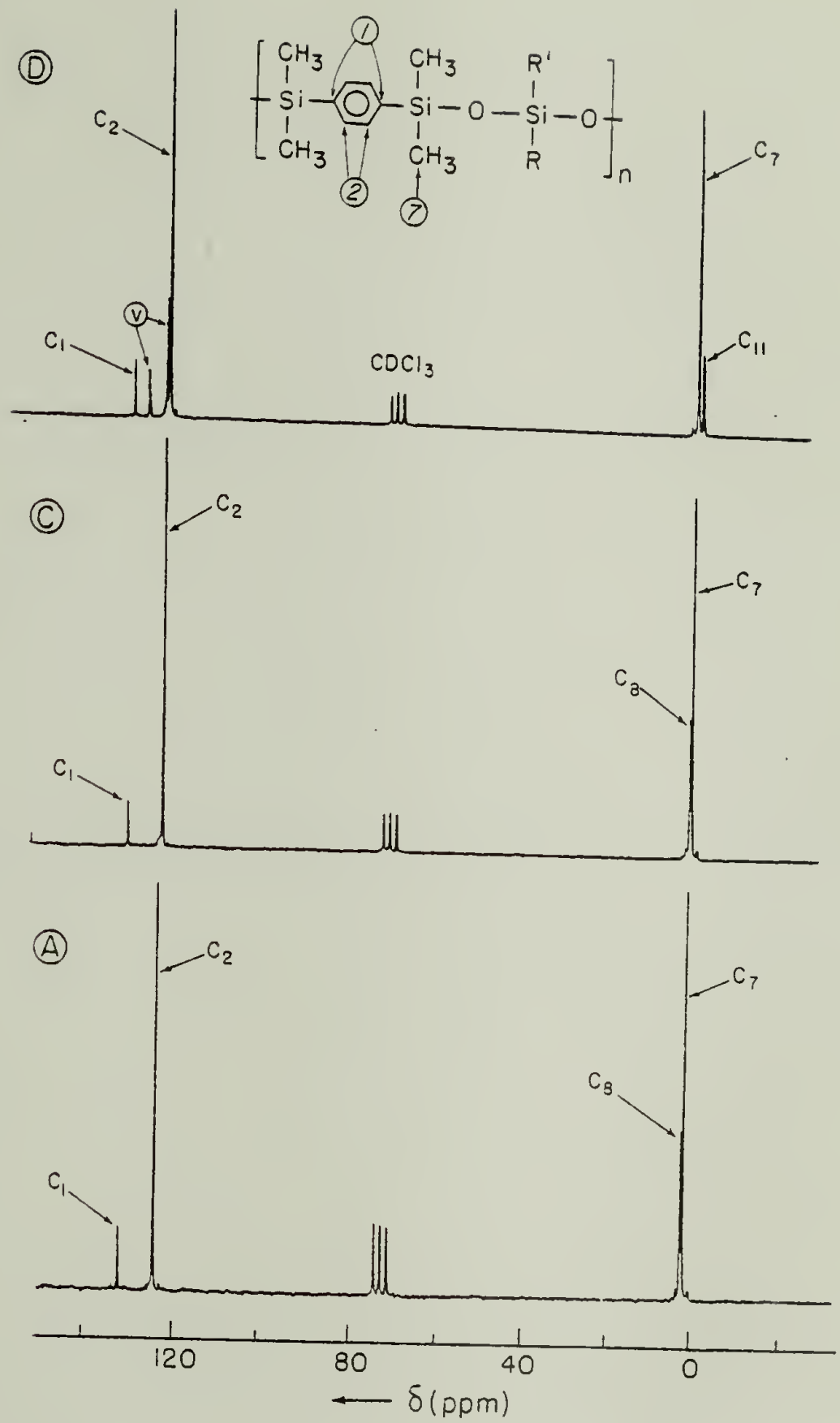


Figure 5-9. ^{13}C NMR spectra of the polymers prepared from the p-diol monomer.

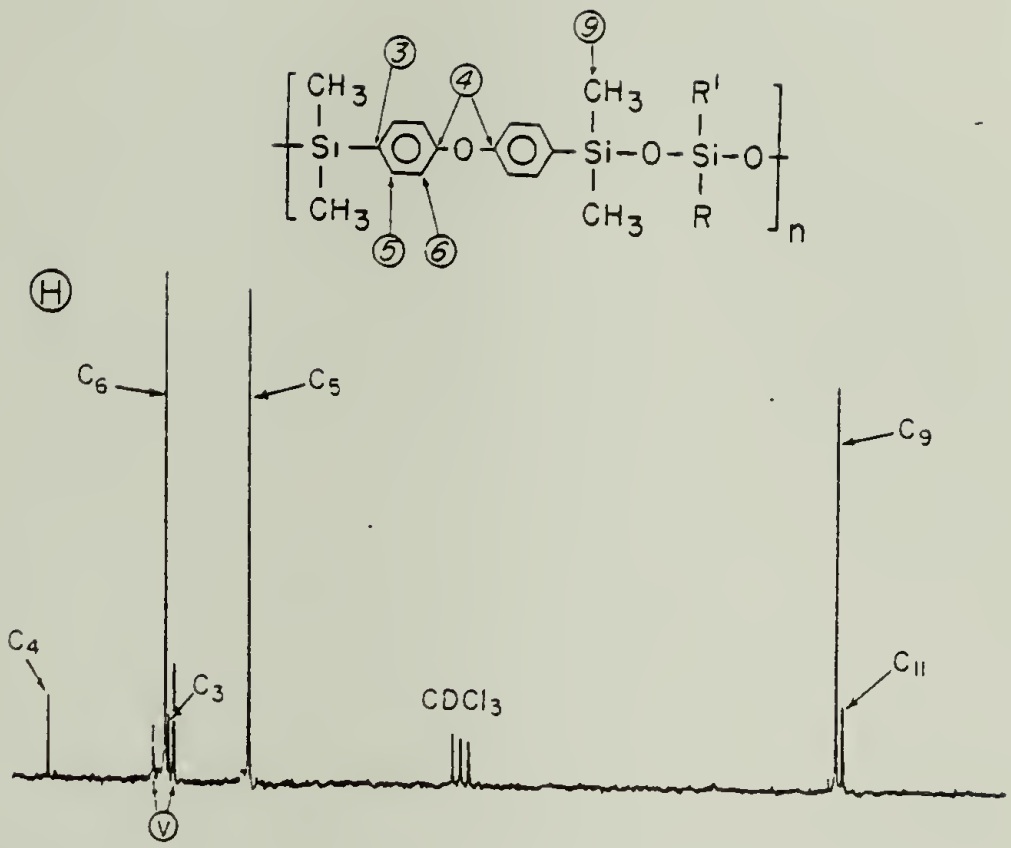


Figure 5-10. ^{13}C NMR spectra of the polymers prepared from the ether-diol monomer.

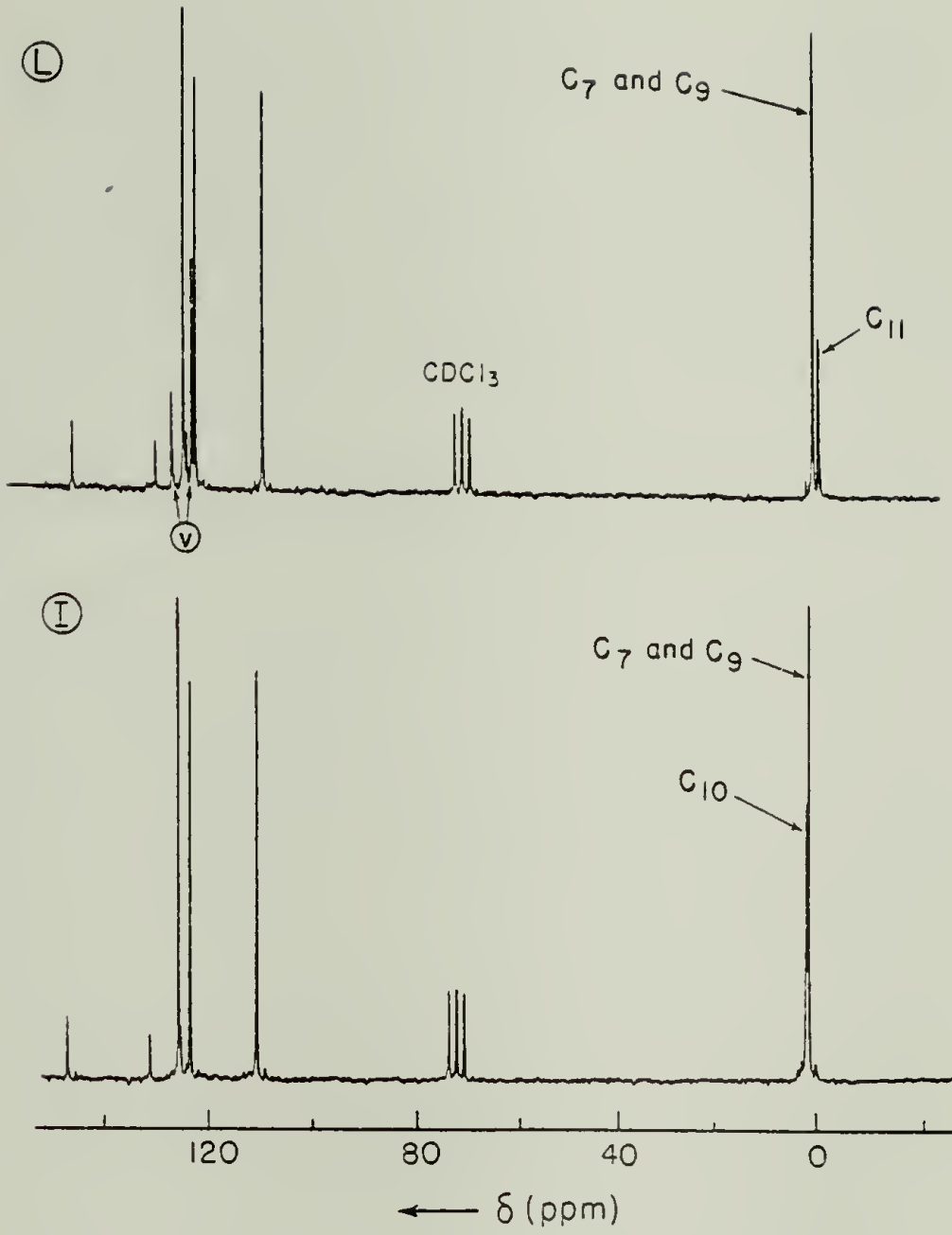


Figure 5-11. ^{13}C NMR spectra of the polymers prepared from a 50 mole % mixture of the two arylenedisilanols.

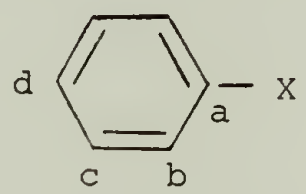
of accepted empirical equations[3,5] in the following way:

a) chemical shifts for aromatic carbons were calculated using the following equation:

$$\delta C_i = 128.5 + \Sigma Z_i \qquad (5\text{-}1)$$

$$(i = a - d)$$

where a, b, c and d refer to the four different carbon atoms in a monosubstituted benzene ring:



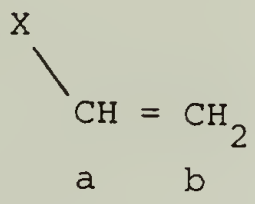
in the case of p-diol polymers, values[3] for Z_i determined for x = $Si(CH_3)_3$ are:

carbon atom	a	b	c	d
Z_i	13.4	4.4	-1.1	-1.1

and in the case of the ether-diol polymers, these values determined for x = $-O-C_6H_4-$ are:

carbon atom	a	b	c	d
Z_i	29.1	-9.5	0.3	-5.3

b) chemical shifts for vinyl carbons were calculated using Equation 5-2 determined for



$$\delta C_i = 123.3 + \Sigma Z_i \qquad (i = a, b) \qquad (5\text{-}2)$$

where for x = $-Si(CH_3)_3$ one finds[3]:

$$Z_a = 16.9 \text{ and } Z_b = 6.7$$

δ values calculated in such a way are listed and compared with observed chemical shifts in Table 5-6.

The following general conclusions could be drawn from the ^{13}C NMR spectra of alternating silarylene-siloxane polymers:

(1) All the polymers showed clear spectra with very sharp peaks and extremely satisfactory signal-to-noise ratios after no more than 10,000 acquisitions. This behavior is highly unusual for carbon-type polymers of comparable high molecular weight, i.e.: $\bar{M}_w$ = 250,000. It is most probably due to two factors: (a) all silarylene-siloxane polymers were very easily soluble in chloroform, thus very desirable high solution concentrations of ~ 10% ($^w/v$) and above were easily attainable, and (b) the extreme flexibility of the chains of these polymers, as was already mentioned in the discussion of ^1H NMR spectra, resulted in sharp, high

TABLE 5-6

Comparison of Calculated and Observed Chemical Shifts in ^{13}C NMR Spectra of Exactly Alternating Silarylene-Siloxane Polymers

Assignment	δ calculated, ppm	δ observed, ppm
C_1	140.8	140.6
C_2	131.8	132.1
C_3	136.6	134.1
C_4	156.5	158.0
C_5	117.9	118.2
C_6	133.2	134.6
C_{12}	140.2	137.1
C_{13}	130.0	133.9

resolution spectra even at high molecular weights.

(2) Thirteen nonequivalent carbon atoms were observed and assigned.

(3) Chemical shifts of the methyl carbon atoms bonded to the silarylene as well as to siloxy silicons were influenced by the nature of the arylene group. This is surprising in the latter case because the methyl carbon on siloxy silicon and the aromatic ring are separated by three chain atoms, e.g.: H_3C-Si-O-Si-C_6H_4, and such a distance seems to be too long for effective interaction. However, it is clearly demonstrated to be so in the example of Polymer I (from a 50 mole % mixture of two arylene disilanols and dimethylureidosilane) in Figure 5-12 and Table 5-5. Two pairs of $-CH_3$ singlets can be seen in Figure 5-12, δ = 1.15 ppm and δ = 0.66 ppm (the silarylene and siloxane methyl carbons, respectively), which agree with the corresponding signals at δ = 1.25 ppm and δ = 0.64 ppm for Polymer A prepared from the pure p-diol, and at δ = 1.26 ppm and δ = 0.74 ppm which agree with the signals at δ = 1.26 ppm and δ = 0.76 ppm for Polymer E prepared from the pure ether-diol.

(4) The methyl carbon atom attached to the silicon atom bearing a vinyl group absorbed at an unusually high field position of δ = -0.52 to -0.60 ppm for Polymers L and D.

(5) It can be seen from Figure 5-9 that Polymer C, which was prepared from the mixture of bisureidosilane monomers containing 7.5 mole % of methylvinyl compound, did not show peaks due to vinyl carbons. However, the same polymer showed vinyl protons in ^1H NMR spectrum (Figure 5-1).

(6) By comparing spectra of the polymers prepared with either pure dimethylureidosilane or pure methylvinylureidosilane but with different

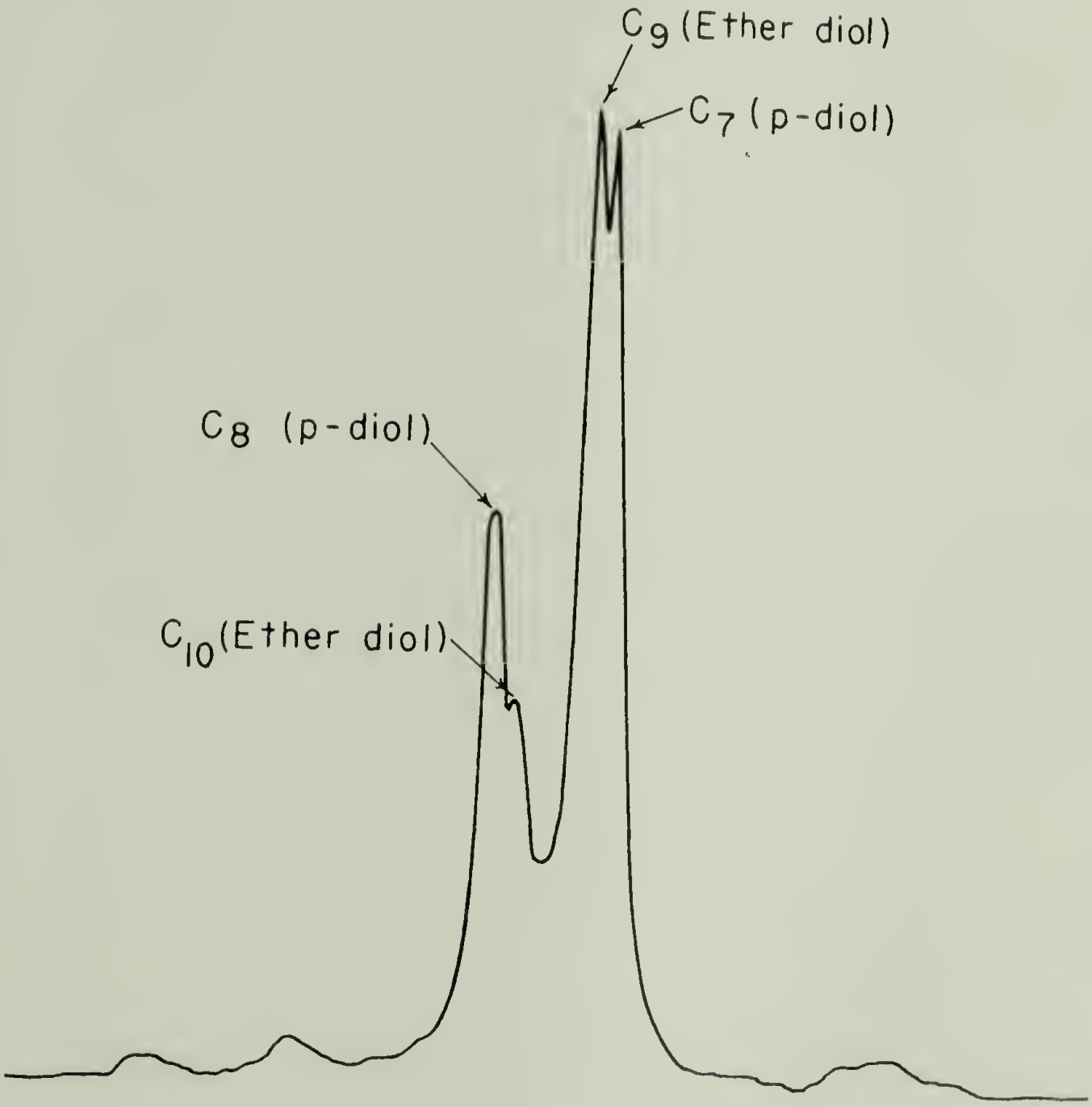


Figure 5-12. Expanded ^{13}C NMR spectrum of the $Si-CH_3$ absorption region of Polymer I.

disilanols or their mixture (Figure 5-7: Polymers A, E and I and Figure 5-8: Polymers D, H and L), it can be seen that a spectrum of the polymer prepared from the mixture of two disilanols represents the summation of the spectra of the polymers from the pure disilanols This confirms that both arylene groups were present in the copolymer, but unfortunately it does not tell anything about the microstructures or arrangements of silarylene groups.

E. Gel Permeation Chromatography (GPC)

In order to estimate molecular weights and polydispersities all of the polymers were examined by GPC. A Waters Gel Permeation Chromatograph, Model 501, with five in-line μ-Styragel crosslinked polystyrene packed columns with pore sizes: 500, 10^3, 10^4, 10^5 and 10^6 Å was used. Tetrahydrofuran was used as the solvent and solutions within a 1-2% ($^w/_v$) concentration range were all carefully filtered before the injections. The calculations were done using a modification of McCaffery's[6] computer program based upon the universal calibration with monodisperse polystyrenes.

As described in the previous chapter, the polymers were isolated from the reaction mixture by filtration of the solution to remove solid urea by-product, followed by dropwise addition into methanol to precipitate the crude polymer. Such a sample was then purified by reprecipitation into methanol from tetrahydrofuran solution. In each of the 12 cases a weight loss was observed while doing this, and it indicated the

existence of low molecular weight fractions which were soluble in tetrahydrofuran-methanol mixtures (1:10 by volume) normally used. This indication was confirmed, for when the liquid phase, which remained after filtering out the reprecipitated polymer, was evaporated to dryness, a small amount of material with a polymeric appearance was observed. To further clarify the situation all three types of products, viz., crude polymers, reprecipitated polymers and low molecular weight fractions from all twelve syntheses were examined by GPC. The results obtained are given in Tables 5-7 to 5-9, and two examples of typical chromatograms for Polymers A and E are shown in Figures 5-13 and 5-14.

The following conclusions could be drawn from these results:
(1) Chromatograms (Figures 5-13 and 5-14) showed a typical binodal distribution with very pronounced low molecular weight tails. The weight average molecular weights of these products were relatively high (above 100,000) but their dispersities were also extraordinarily high (as high as 10.5 in Table 5-7) and far from those predicted and usually found for condensation polymerization reaction products which usually have the most probable distribution[7] with $\bar{M}_w/\bar{M}_n = 2.0$.
(2) Crude polymers can easily be fractionated by the simple reprecipitation procedure already described. They separated into a high molecular weight fraction, which corresponds to the reprecipitated polymer, and a low molecular weight fraction, which was soluble in 10:1 (v/v) methanol-tetrahydrofuran mixture.

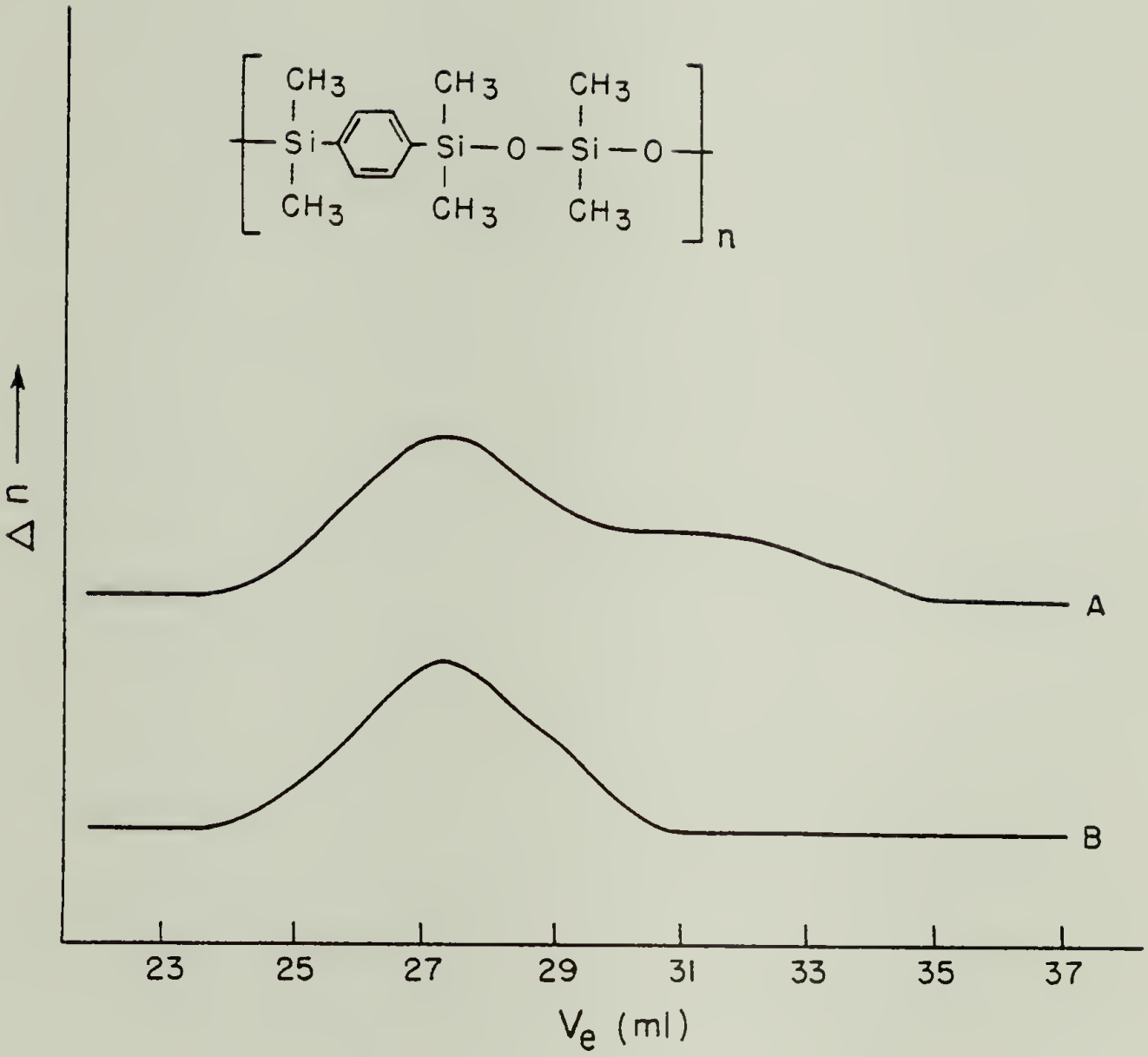


Figure 5-13. GPC curves obtained for Polymer A.

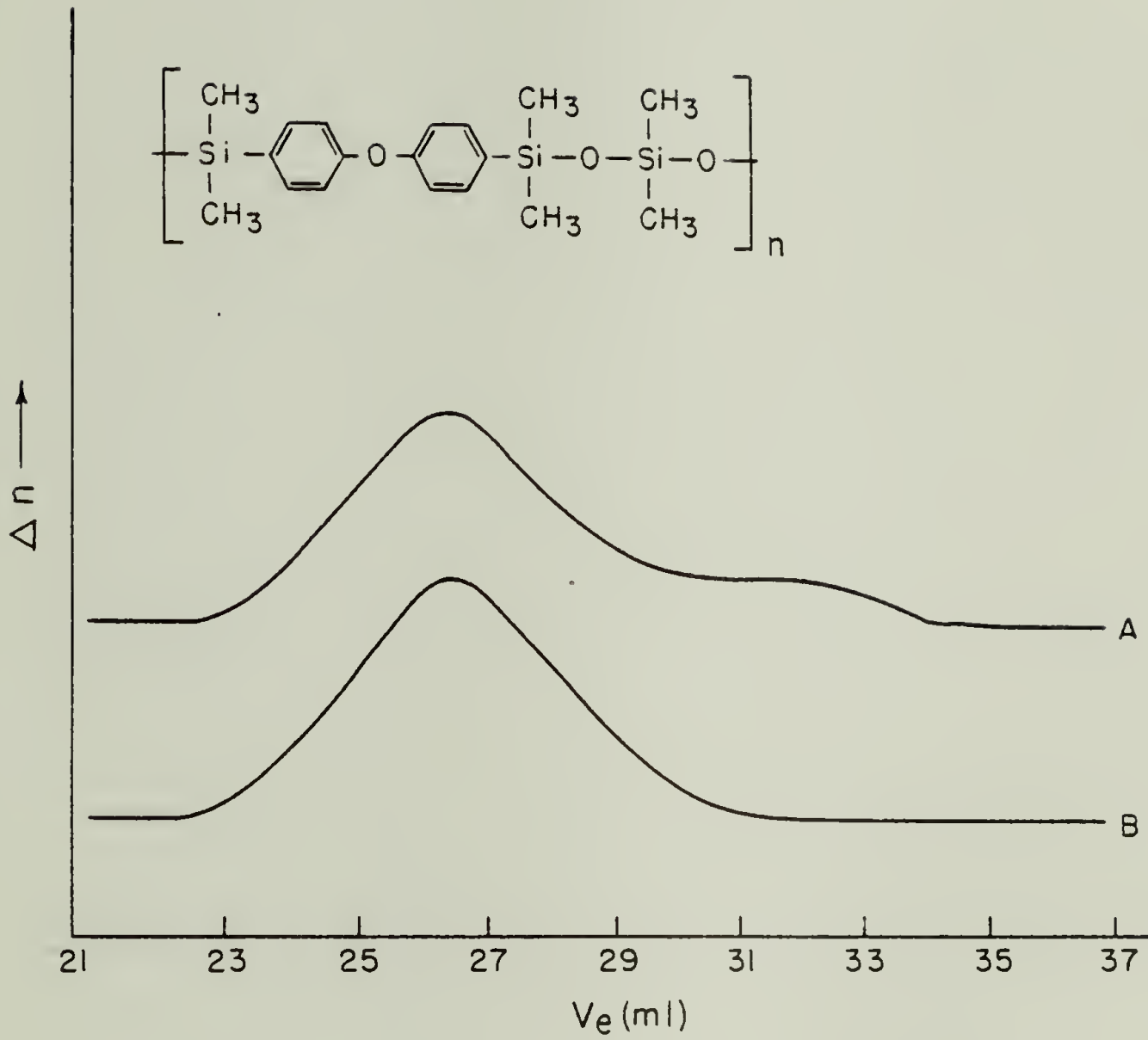


Figure 5-14. GPC curves obtained for Polymer E.

TABLE 5-7

Molecular Weights and Polydispersities of Crude Alternating Silarylene-Siloxane Polymers

Polymer	Disilanol	vinyl content, %	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A	p-diol	0	14 000	125 000	8.90
B		5	51 000	107 000	2.10
C		7.5	49 000	116 500	2.38
D		100	14 000	145 500	10.27
E	ether-diol	0	22 500	176 500	7.87
F		5	6 500	67 500	10.49
G		7.5	25 500	152 000	5.99
H		100	48 500	205 500	4.25
I	50 mole % mixture	0	55 000	155 000	2.81
J		5	25 000	215 000	8.70
K		7.5	41 500	136 000	3.27
L		100	71 500	182 500	2.55

TABLE 5-8

Molecular Weights and Polydispersities of Reprecipitated Alternating Silarylene-Siloxane Polymers as Determined by GPC

Polymer	Disilanol	vinyl content, %	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A	p-diol	0	71 500	132 000	1.86
B		5	67 000	119 000	1.78
C		7.5	69 000	125 500	1.81
D		100	103 500	199 000	1.92
E	ether-diol	0	100 500	214 000	2.13
F		5	40 000	74 000	1.86
G		7.5	103 500	184 000	1.78
H		100	143 000	232 000	1.63
I	50 mole % mixture	0	88 000	163 000	1.86
J		5	126 000	239 500	1.89
K		7.5	92 500	164 500	1.78
L		100	128 500	218 500	1.70

TABLE 5-9

Molecular Weights and Polydispersities of Low Molecular Weight Fractions of Alternating Silarylene-Siloxane Polymers

Polymer	Disilanol	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A	p-diol	3753	11496	3.06
B		4740	8918	1.88
C		8358	14451	1.73
D		5824	14804	2.54
E	ether-diol	7175	8999	1.25
F		25295	34387	1.36
G		4722	21479	4.55
H		31150	24599	1.87
I	50 mole % mixture	3212	10881	3.39
J		656	2035	3.10
K		21434	30370	1.42
L		11392	15253	1.34

(3) Reprecipitated polymers showed molecular weight distribution patterns typical for products of a condensation polymerization reaction with a polydispersity close to two. Weight average molecular weights as high as 240,000 were obtained (Table 5-8).

(4) Most of the low molecular weight samples showed weight average molecular weights between 10,000 and 30,000. Their polydispersities were also very close to two indicating that these fractions obeyed the laws of condensation polymerization reaction.

(5) The reason for such distribution patterns most probably lies in the technique used to prepare the polymers. Condensation polymerizations were performed by addition of a solution of the bisureidosilane to the arylenedisilanol, as described in Chapter IV. This addition was monitored by either ^{1}H NMR or GPC, and it was stopped when the first excess of unreacted ureidosilane was observed. At that point all silanol functional groups had reacted and all of the polymer chains were terminated with ureido functional groups. In such a system the condensation polymerization reaction was then completed. To use up the excess ureidosilane monomer and endgroups and further increase polymer molecular weight, a small amount of arylenedisilanol was then added. This amount was predetermined by the monitoring technique used. On the basis of the GPC results discussed, it seems that a new condensation reaction may have been started between the excess of ureidosilane monomer and the added arylenedisilanol within the system in which one condensation polymerization reaction had already ended. Probably because of

the small amounts of monomers involved in this new reaction and the relative inaccuracy of measurement of amounts at this concentration, a polymeric product described here as a crude polymer, which was composed of two fractions with extremely different molecular weights, was consequently formed.

(6) Finally, the GPC analyses clearly demonstrated that the synthetic procedure developed in this work was capable of producing high molecular weight polymers.

F. Dilute Solution Viscometry

Intrinsic viscosities of dilute polymer solutions[8] were determined in tetrahydrofuran at 30±0.5°C using an Ubbelohde dilution viscometer (Cannon Model 25D703). In all determinations the concentrations of original solutions ranged from 0.57g/dl to 0.51g/dl and flow times were measured at five different dilutions. The intrinsic viscosities obtained in such a manner are listed in Table 5-10.

The following conclusions could be drawn from these measurements:

(1) The intrinsic viscosities of all polymers ranged between 0.36 dl/g and 0.70 dl/g and were reproducible within 5%.

(2) With the exception of Polymer A, the values for the Mark-Houwink constants for these polymers were not known. Using $K = 7.86, .10^{-5}$ and $a = 0.757$[9] for Polymer A, the calculated value for $\bar{M}_v$ was 112,700, which agreed with the $\bar{M}_w$ value obtained for the same polymer

TABLE 5-10

Intrinsic Viscosities of Alternating Silarylene-Siloxane Polymers

Polymer	Disilanol	Vinyl Content, %	[η], dl/g
A	p-diol	0	0.524
B		5	0.443
C		7.5	0.461
D		100	0.623
E	ether-diol	0	0.667
F		5	0.308
G		7.5	0.525
H		100	0.692
I	50 mole % mixture	0	0.582
J		5	0.681
K		7.5	0.497
L		100	0.692

by GPC (Table 5-8).

(3) For the other polymers it was difficult to establish the correlation between the intrinsic viscosity values and GPC results. However, it seems that within each of the three groups of polymers the order of increasing values of [η] followed the order of increasing $\bar{M}_w$ as determined by GPC. Unfortunately, nothing can be concluded at present about the absolute values of the molecular weights without basic fractionation studies and the determination of Mark-Houwnik constants for each polymer.

G. Differential Scanning Calorimetry (DSC)

To determine the transition temperatures of the polymers a Perkin Elmer Differential Scanning Calorimeter, Model DSC-2, was used. In all cases a temperature interval between -100°C and 250°C was covered by two different heating rates: 20°C/min and 5°C/min. The samples analyzed ranged from 15 to 25mg in weight and a maximum sensitivity of 2 mcal/sec was used. For subambient runs liquid nitrogen was employed as a cooling fluid.

1. Glass Transition Temperatures

To determine the glass transition temperatures of the alternating silarylene-siloxane polymers, a temperature range between -100°C and 25°C was covered. The results obtained are presented in Table 5-11. To illustrate further this behavior a thermogram which compares polymers

TABLE 5-11

Glass Transition Temperatures of Alternating Linear Silarylene-Siloxane Polymers

Diol Monomer	Vinyl Monomer, %	Polymer Sample	T_g, °C at 20°/min.	T_g, °C at 5°/min.	Calcd. T_g, °C
p-diol	0	A	-62	-64	
	5	B	-63	-65	-62
	7.5	C	-63	-66	-63
	100	D	-69	-72	
ether-diol	0	E	-24	-26	
	5	F	-25	-26	-24
	7.5	G(P)	-25	-26	-27
	100	H	-34	-27	
50 mole % mixture	0	I	-42	-43	-42
	5	J	-43	-44	-42
	7.5	K	-44	-47	-43
	100	L	-51	-53	-50

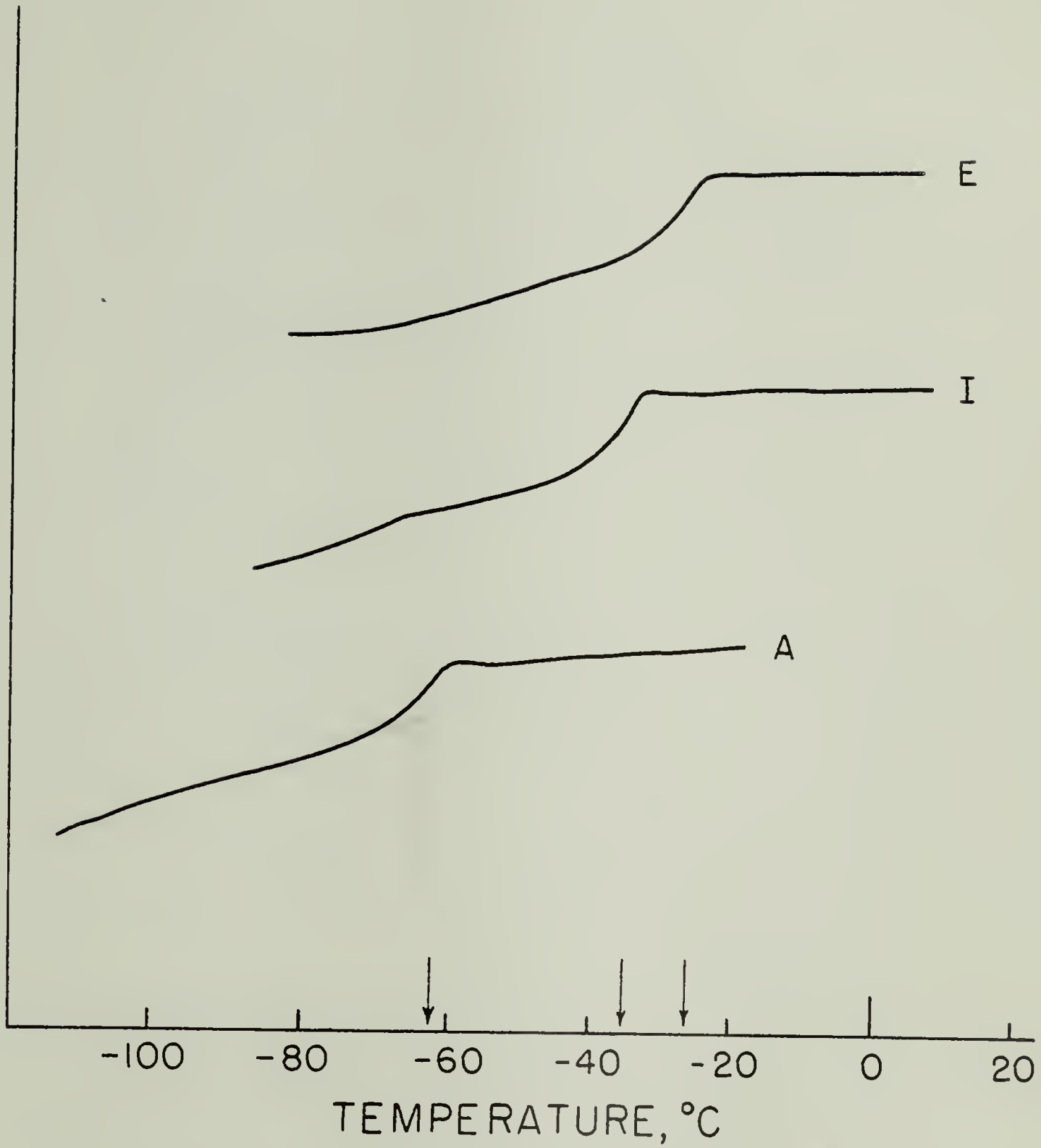


Figure 5-15. Glass transition temperatures of exactly alternating silarylene-siloxane polymers prepared from dimethylureidosilane and the following arylenedisilanols: A: p-diol; E: ether-diol; and I: 50 mole % mixture of the two diols.

prepared from different arylenedisilanols with dimethylureidosilane (Polymers A, E and I) is shown in Figure 5-15.

As already discussed in Chapter I, there has been a controversy over the years concerning the glass transition temperature of poly[1,4-bis-(oxydimethylsilyl)benzene dimethylsilane], which is Polymer A according to the denotation used here. Two distinctly different values were reported in the literature. First, in 1967, L.W. Breed[10] predicted (although he never synthesized the polymer) the value of -53°C. Six years later, when the polymer for the first time was actually prepared[11] R.E. Burks reported its glass transition temperature (by DSC) to be -63°C. This finding was confirmed three years later by C.U. Pittman, Jr., W.J. Patterson and S.P. McManus[19], who found T_g = -62°C by both DSC and torsional braid analysis (TBA), and they suggested that the value predicted by Breed "should be reconsidered." From Table 5-14 it can be seen that the glass transition temperature determined in the present work by DSC depended on the heating rate. The heating rates used by previous workers were not reported, but the T_g for Polymer A which was obtained in this work at a heating rate of 20°C/min is -62°C in accordance with the value reported by Pittman and coworkers. It is noteworthy that in these three independent investigations, Polymer A or its equivalent, was synthesized by two entirely different chemical reactions (compare Chapter I and Chapter IV), but in all cases the polymer showed the same value for the glass transition temperature.

In addition to this result the following conclusions and observations can be drawn from these measurements:

(1) The glass transition temperatures of the copolymers were calculated using the Gordon-Taylor equation[13,14], and the results are compared with the experimentally obtained values in Table 14. The equation is:

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} \qquad (5\text{-}3)$$

where: T_g (°K) is the glass transition temperature of the copolymer; T_{g_1} (°K) and T_{g_2} (°K) are the glass transition temperatures of the pure homopolymers 1 and 2; and W_1 and W_2 are the weight fractions of repeating units 1 and 2 in the copolymer. For these calculations Polymers A and D were taken as the reference homopolymers. It can be seen from the data in Table 5-11 that the experimentally obtained values for the polymer glass transition temperatures are almost exactly those predicted by Equation 5-3.

(2) Incorporation of the vinyl silane group into the copolymer resulted in a substantial decrease in the glass transition temperatures of the copolymers from both types of arylenedisilanol monomers, as well as for their mixture. It is known in many cases[12,13,14] that the presence of large and bulky groups pendant to the polymer chain generally increases the glass transition temperature of the material by decreasing the interchain free volume and thus restricting the overall mobility of the segments at lower temperatures. From this viewpoint the behavior

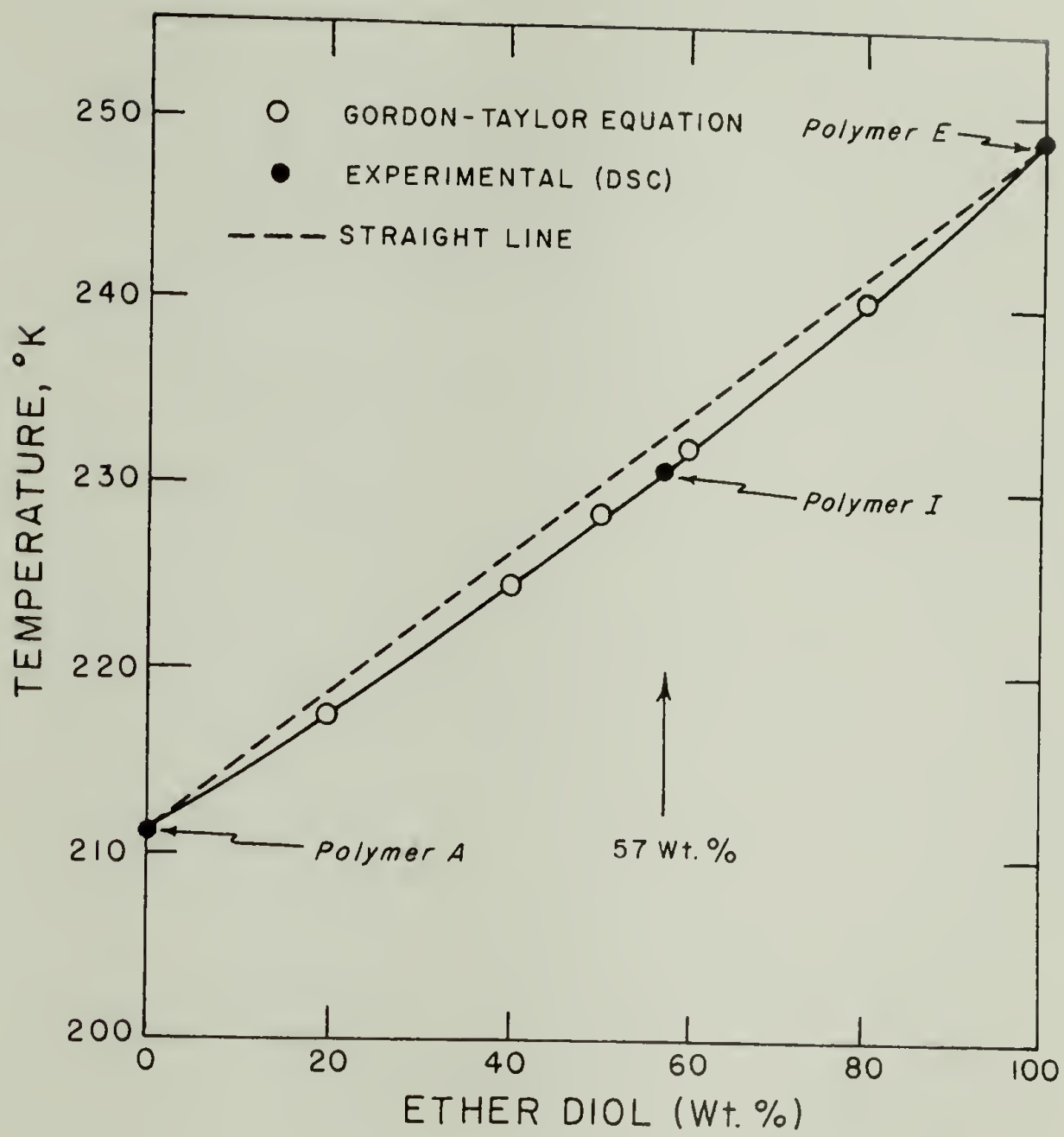


Figure 5-16. Comparison of calculated and experimentally obtained T_g values for the polymers prepared from dimethylureidosilane.

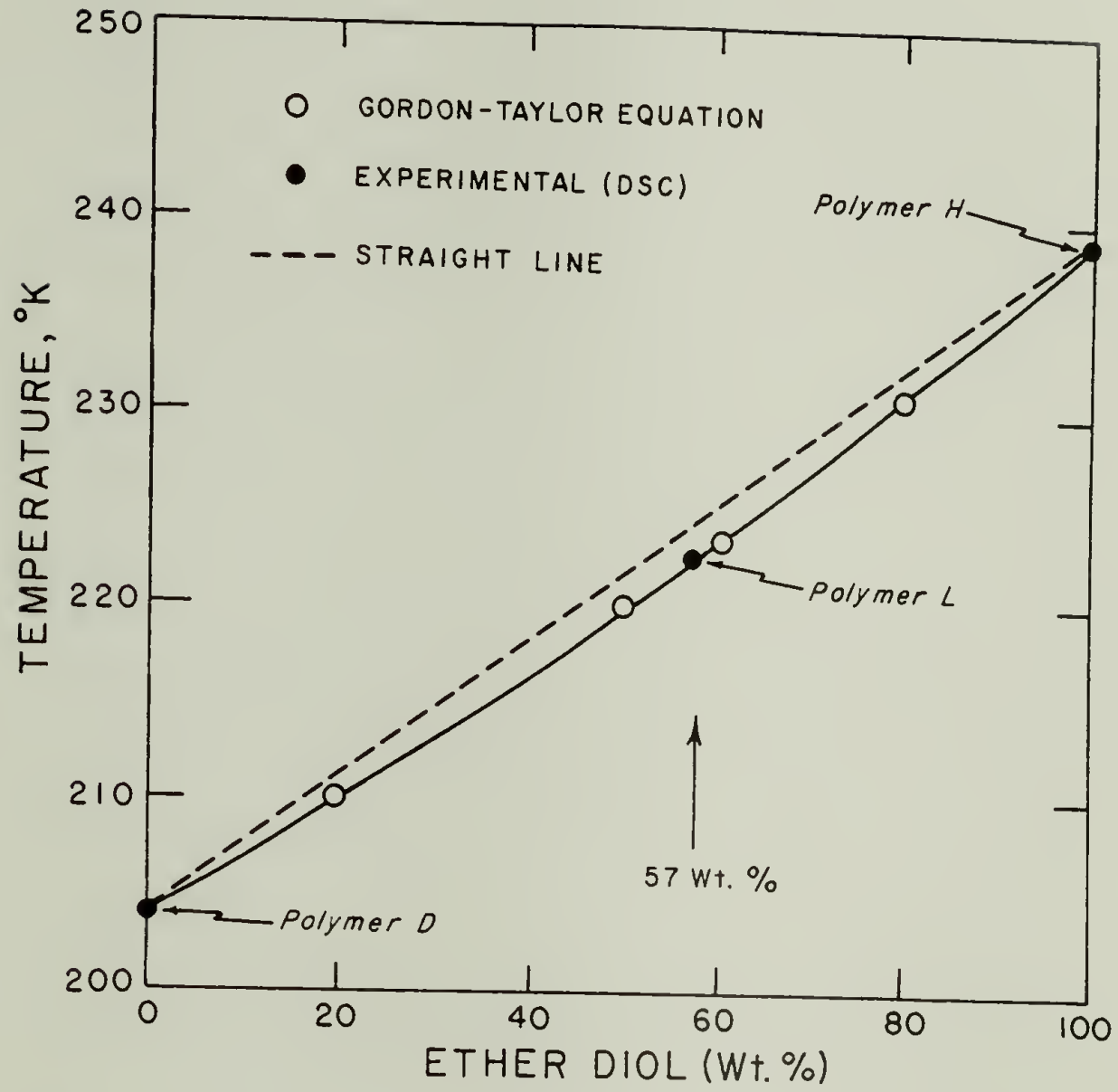


Figure 5-17. Comparison of calculated and experimentally obtained T_g values for the polymers prepared from methylvinylureidosilane.

demonstrated by the alternating silarylene-siloxane copolymers containing vinyl groups might be unexpected. Apparently, the pendant vinyl groups act to plasticize the polymer rather than to hinder free rotation.

(3) Of the two types of polymers, these from p-diol monomer (Polymers A-D) had the most attractive T_g values for an elastomer. As seen in Table 5-11, the T_g values of these polymers were about 40° lower than those of the polymers from the ether-diol monomer (Polymers E-H). It is possible that the T_g values of the latter polymers might be too high for good elastomeric properties at room temperature, but investigations of the mechanical and viscoelastic properties of all these polymers will be necessary to determine if such is the case. However, the glass transition temperatures below -60°C of the p-diol homopolymers and copolymers certainly are in a very attractive range for good elastomeric properties at room temperature and below.

2. Melting Behavior

All of the alternating silarylene-siloxane polymers were opaque, highly viscous liquids. Such appearance suggests the existence of some degree of crystallinity in them. To determine if this was the case differential scanning calorimetry and variable temperature infrared spectrometry were used. The following observations were made:

(1) DSC did not show conclusively the presence of a melting endotherm within the temperature interval of 25°C to 250°C. Even when unusually large samples were run at very high sensitivities, nothing suspecting

a melting behavior could be seen.

(2) On the other hand some results obtained during the initial period of this work by variable temperature infrared spectrometry indicated that there might be some crystallinity, at least in the polymers prepared from the p-diol monomer. It was observed that the infrared absorption bands at 1240-1260, 1050, 780-790 and 650 cm^{-1} reversibly disappeared and reappeared, as shown in Figure 5-18, when the samples were heated from 25°C (spectrum a) to 125°C (spectrum b) and cooled back again. This observation might indicate the existence of some crystallinity within the polymers, if these bands can be assigned to crystalline regions.

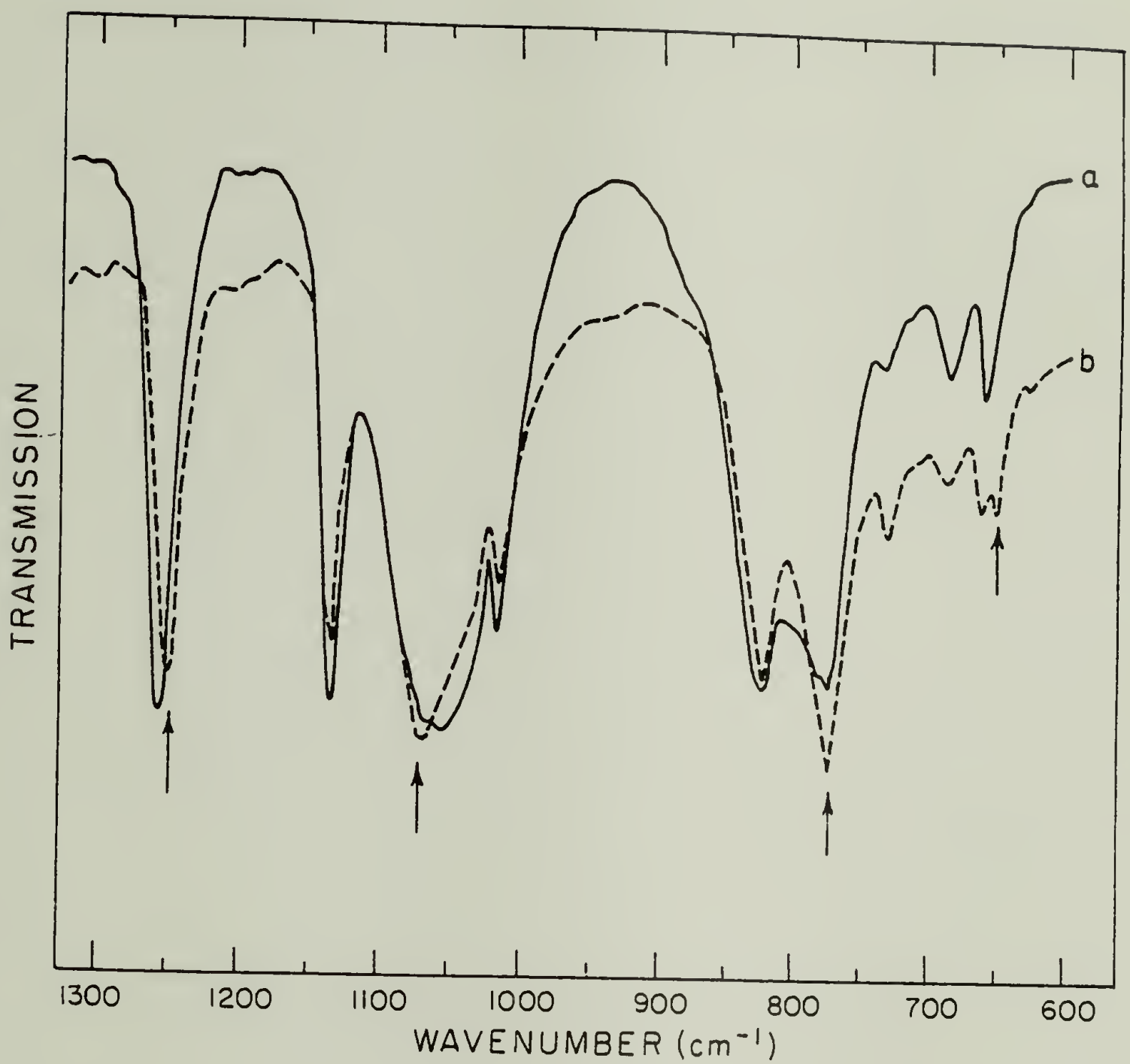


Figure 5-18. IR spectra of Polymer A at various temperatures: a: at 25°C and b: at 125°C.

Bibliography

1. F.A. Bovey, "High Resolution NMR of Macromolecules", Academic Press, New York (1972); p. 14.
2. R.M. Silverstein, G.C. Bassler, "Spectrometric Identification of Organic Compounds", John Wiley and Sons Inc., New York (1967); p. 64.
3. E. Pretsch, T. Clerc, J. Seibl, W. Simon, "Tabellen zur Strukturaufklarung organischer Verbindungen", Springer-Verlag, Berlin (1967); p. C90 and C120.
4. N. Koide, private communication
5. E. Breitmaier, W. Voelter, "^{13}C NMR Spectroscopy", 2nd edition, Verlag-Chemie, Weinheim-New York (1978); p. 183.
6. E.M. McCaffery, "Laboratory Preparation for Macromolecular Chemistry", McGraw-Hill, New York (1970); p. 368.
7. P.J. Flory, "Principles of Polymer Chemistry", Cornell University Press (1971); p. 321.
8. E.A. Collins, J. Bares, F.W. Billmeyer, Jr., "Experiments in Polymer Science", Interscience, New York (1973); p. 147.
9. C.U. Pittman, Jr., W.J. Patterson, S.P. McManus, "Oxysilane Polymers from Silanediol-Bisdimethylaminosilane Polycondensations: Synthesis and Properties", J. Polymer Sci., Polymer Chem. Ed., 14, 1715 (1976).
10. L.W. Breed, R.L. Elliott, M.E. Whitehead, "Arylene-Modified Siloxanes", J. Polymer Sci., A-1, 5, 2745 (1967).

11. R.E. Burks, Jr., E.V. Covington, M.V. Jackson, J.E. Curry, "Copolymers and Elastomers with Alternating Dioxysilphenylene and Silane Units", J. Polymer Sci., Polymer Chem. Ed., 11, 319 (1973).

12. J.J. Aklonis, W.J. MacKnight, M. Shen, "Introduction to Polymer Viscoelasticity", Wiley-Interscience, New York (1972); p. 80.

13. P. Mears, "Polymers: Structure and Bulk Properties", D. Van Nostrand Company Ltd. (1967); p. 262.

14. E.A. Dimarzio, J.H. Gibbs, "Molecular Interpretation of Glass Temperature Depression by Plasticizers", J. Polymer Sci., A, 1, 1417 (1963).

C H A P T E R V I

THERMAL STABILITY AND DEGRADATION OF EXACTLY ALTERNATING SILARYLENE-SILOXANE POLYMERS

A. Introduction

As discussed in Chapter I, the high thermal stability[1] in air as well as in inert atmosphere and the excellent elasticity at low temperatures are the properties that make siloxane polymers highly desirable. It was already pointed out that the exactly alternating silarylene-siloxane polymers were expected to show even better high temperature stability while retaining (as shown in Chapter V) good low temperature properties. In test to check this expectation, the stability and degradation of these polymers were examined by both Thermogravimetric Analysis[2] and controlled pyrolysis. This chapter describes the methods and instrumentation used for these purposes and the interpretation, to the best of our present understanding, of the information obtained.

B. Thermogravimetric Analysis (TGA)

All the polymers were subjected to thermal degradation in air and in nitrogen. A Du Pont 950 Thermogravimetric Analyzer in line with a Du Pont 900 Thermal Analyzer was used. The sample weights ranged from

10 to 15 mg. and they were heated at a rate of 15°C/min. The results obtained are presented in Tables 6-1 and 6-2 and the thermograms are shown in Figures 6-1 through 6-10.

The following conclusions could be drawn from these data:

(1) The mechanisms of degradation in air (Figures 6-1 to 6-5) and in nitrogen (Figures 6-6 to 6-10) were entirely different in nature. While decomposition by a single process apparently occurred in nitrogen, in air a three-step process seemed to be involved.

(2) In almost all cases degradation started at lower temperatures in air than in nitrogen.

(3) With the exception of polymers prepared from methylvinylureidosilane and Polymer C, a 50% weight loss was achieved at lower temperatures in a nitrogen atmosphere than in air.

(4) Vinyl substituted polymers were more stable than the dimethylsiloxane polymers and resistance to thermal degradation apparently increased with increasing vinyl content as seen in Figures 6-3 through 6-5 and 6-8 through 6-10 for degradation in air and nitrogen, respectively.

(5) In nitrogen, polymers from the ether-diol monomer were more stable than those from p-diol monomer and while the copolymer from the 50 mole % diol mixture was in between, the situation was reversed in air, as seen in Figures 6-1 and 6-6.

(6) The first step of the degradation in air was characterized by only a small weight loss which in no case exceeded 5 wt % (Table 6-3). The

TABLE 6-1

TGA in Air of Exactly Alternating Silarylene-Siloxane Polymers

Polymer	Disilanol	Vinyl Content, %	Onset of degrad., °C	Temp. for 50% wt. loss, °C	End of degrad., °C	Wt. remained, %
A	p-diol	0	345	665	735	39.5
B		5	370	705	730	46
C		7.5	375	725	730	49.5
D		100	420	-	725	58.5
E	ether-diol	0	335	610	720	26.5
F		5	370	620	740	32
G		7.5	410	630	720	35
H		100	425	675	730	41
I	50 mole % mixture	0	360	635	730	37
J		5	390	670	725	40.5
K		7.5	405	660	720	42
L		100	420	670	730	46

TABLE 6-2

TGA in Nitrogen of Exactly Alternating Silarylene-Siloxane Polymers

Polymer	Disilanol	Vinyl Content, %	Onset degrad., °C	Temp. for 50% wt. loss, °C	End of degrad., °C	Wt. remained, %
A	p-diol	0	400	545	660	30.5
B		5	360	580	670	41
C		7.5	420	-	680	51
D		100	450	-	690	75
E	ether-diol	0	470	520	650	33
F		5	420	590	690	38.5
G		7.5	465	600	720	43
H		100	490	-	740	66.5
I	50 mole % mixture	0	390	530	750	31.5
J		5	430	620	760	40.5
K		7.5	420	625	770	42.5
L		100	415	-	785	59

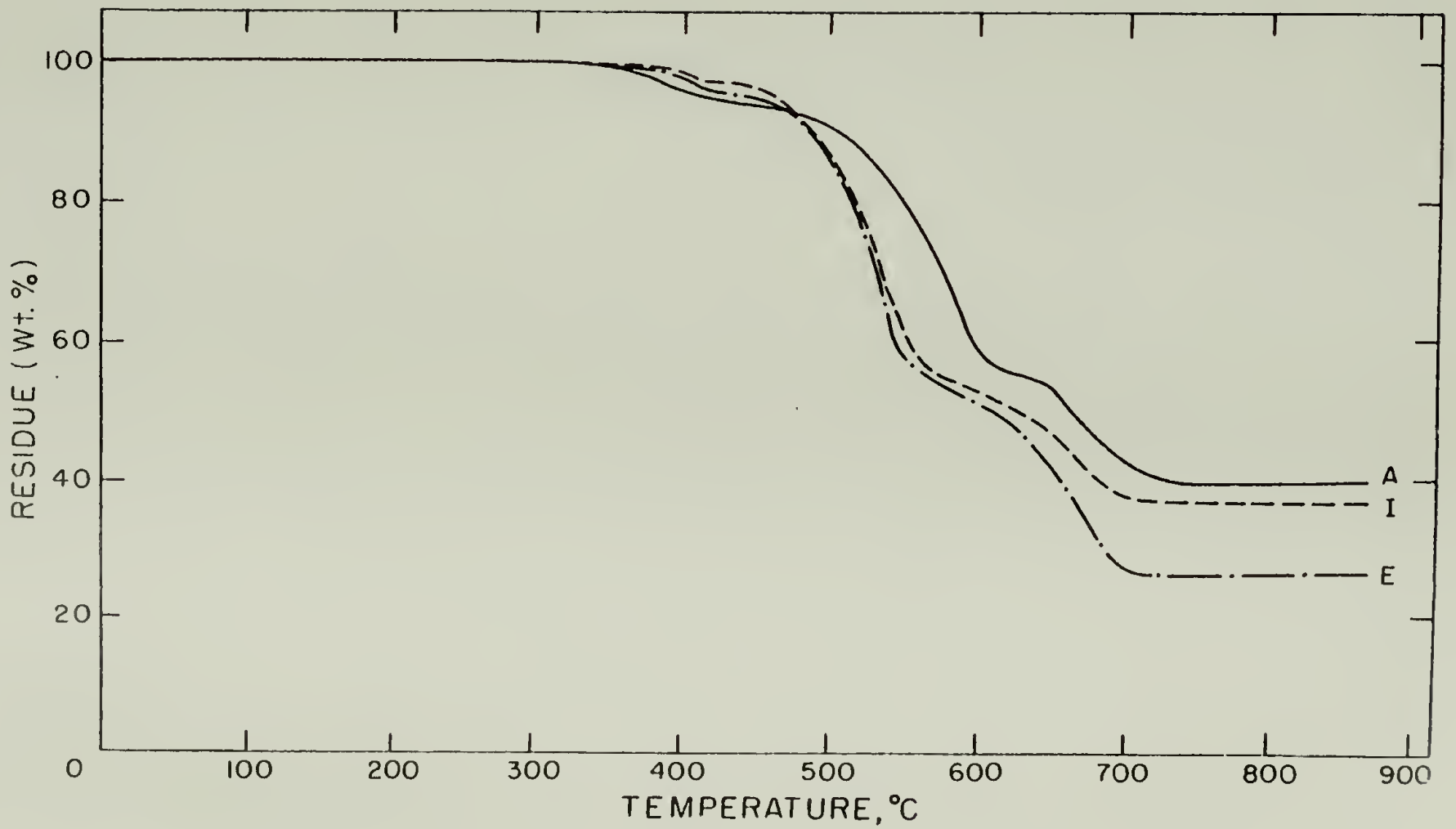


Figure 6-1. TGA in air for silarylene-dimethylsiloxane polymers containing the following silarylene units: A: p-diol; E: ether-diol; I: 50 mole % mixture.

Figure 6-2. TGA in air for silarylene-methylvinylsiloxane polymers containing the following arylene units: D: p-diol; L: ether-diol; H: 50 mole % mixture.

Figure 6-3. TGA in air for p-diol silarylene-siloxane polymers containing the following amount of methylvinylsiloxane units: A: 0%; B: 5%; C: 7.5%; D: 100%.

Figure 6-4. TGA in air for ether-diol silarylene-siloxane polymers containing the following amount of methylvinylsiloxane units: E: 0%; F: 5%; G: 7.5%; H: 100%.

Figure 6-5. TGA in air for the silarylene-siloxane polymers prepared from a 50 mole % mixture of the two disilanols and containing the following amount of methylvinylsiloxane units: I: 0%; J: 5%; K: 7.5%; L: 100%.

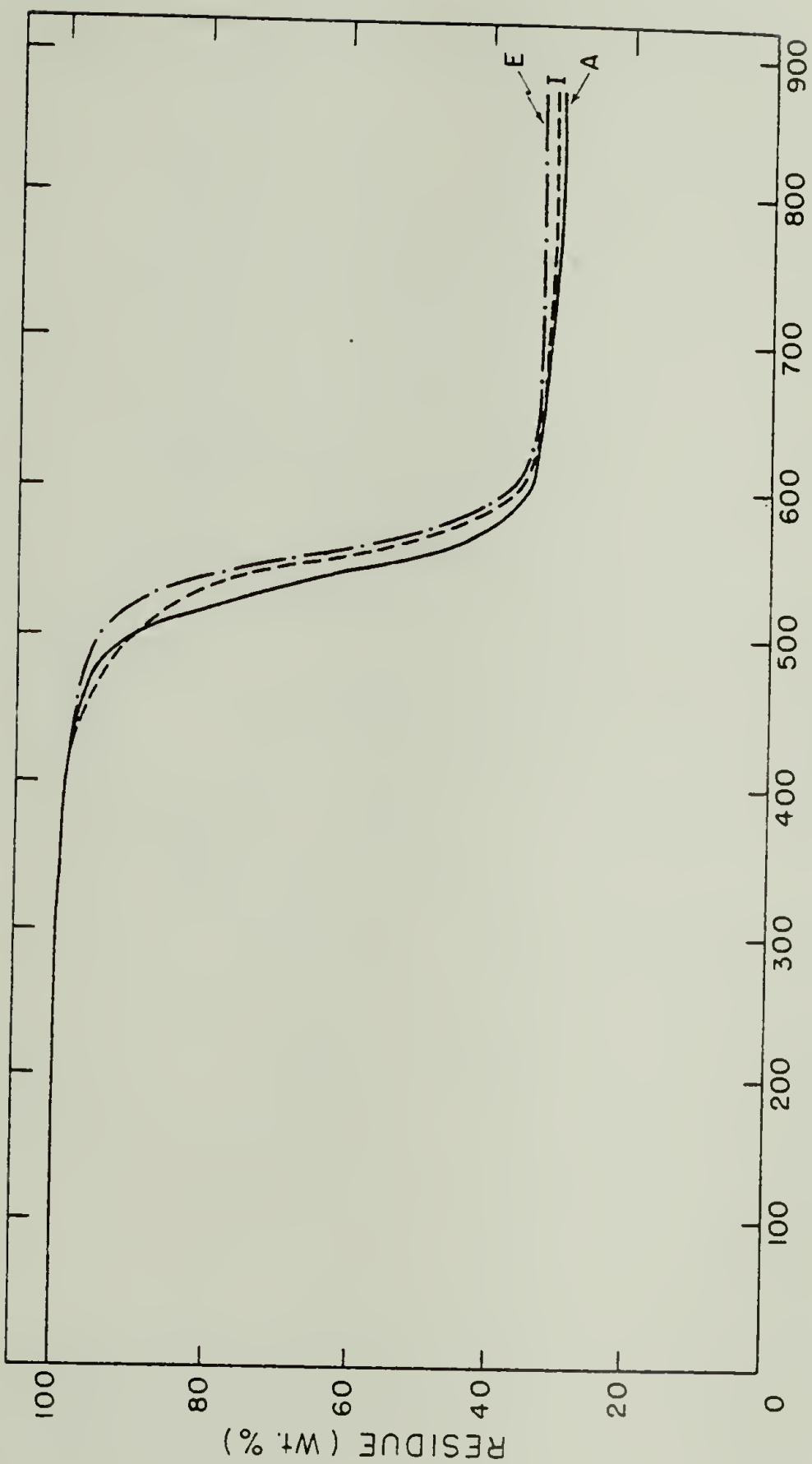


Figure 6-6. TGA in nitrogen for silarylene-dimethylsiloxane polymers containing the following silarylene units: A: p-diol; E: ether-diol; I: 50 mole % mixture.

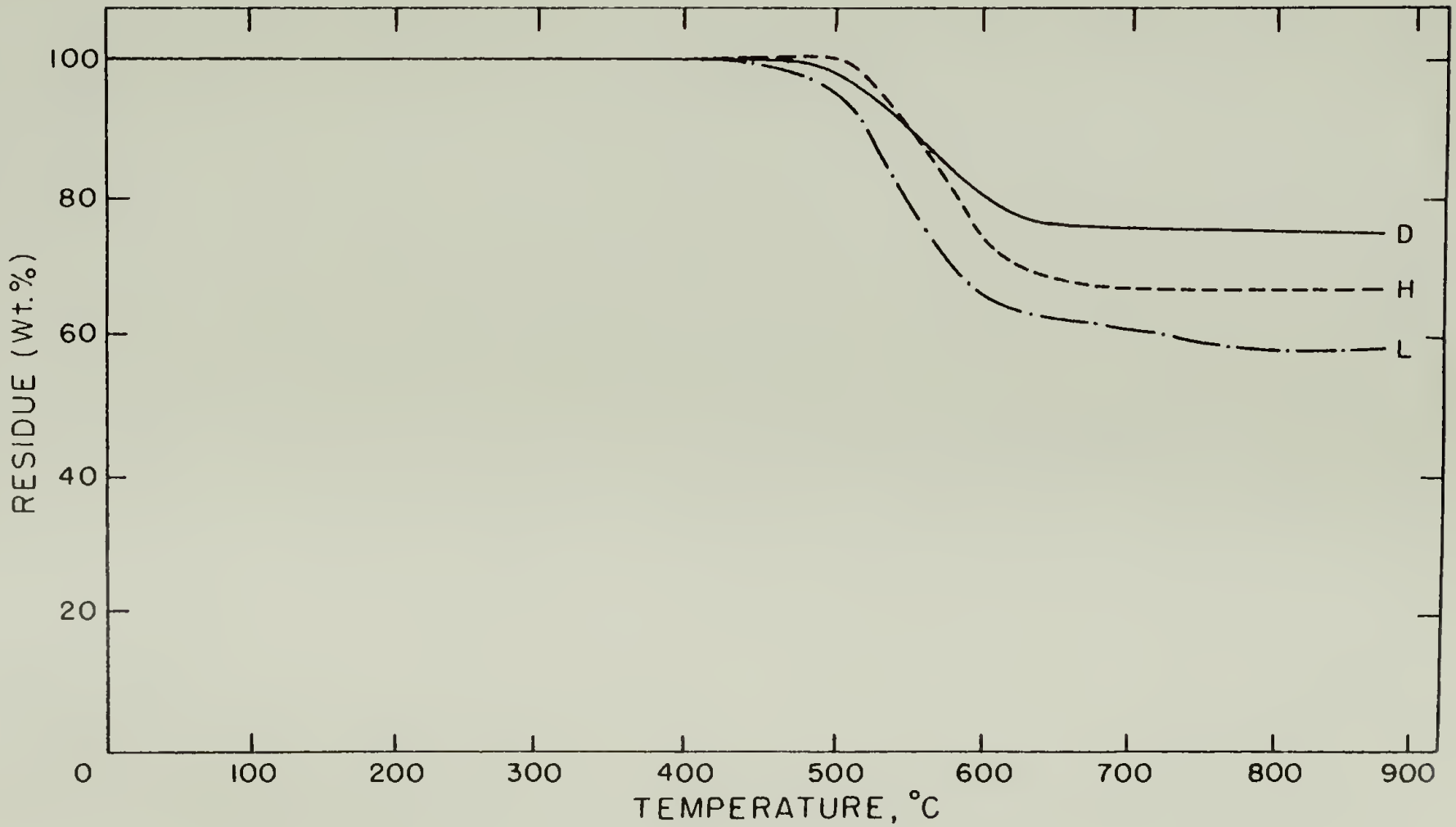


Figure 6-7. TGA in nitrogen for silarylene-methylvinylsiloxane polymers containing the following silarylene units: D: p-diol; H: ether-diol; L: 50 mole % mixture.

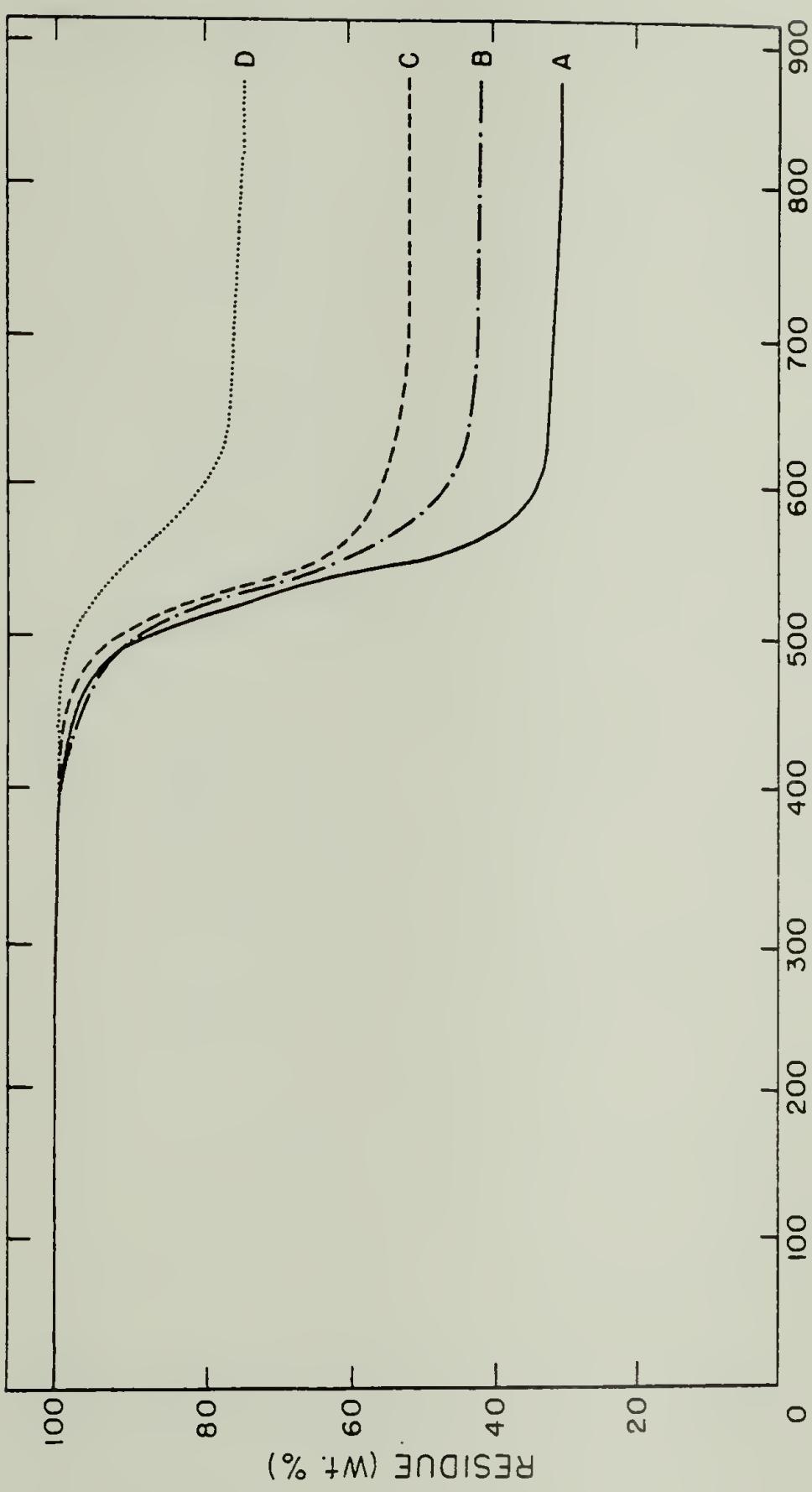


Figure 6-8. TGA in nitrogen for p-diol silarylene-siloxane polymers containing the following amount of methylvinylsiloxane units: A: 0%; B: 5%; C: 7.5%; D: 100%.

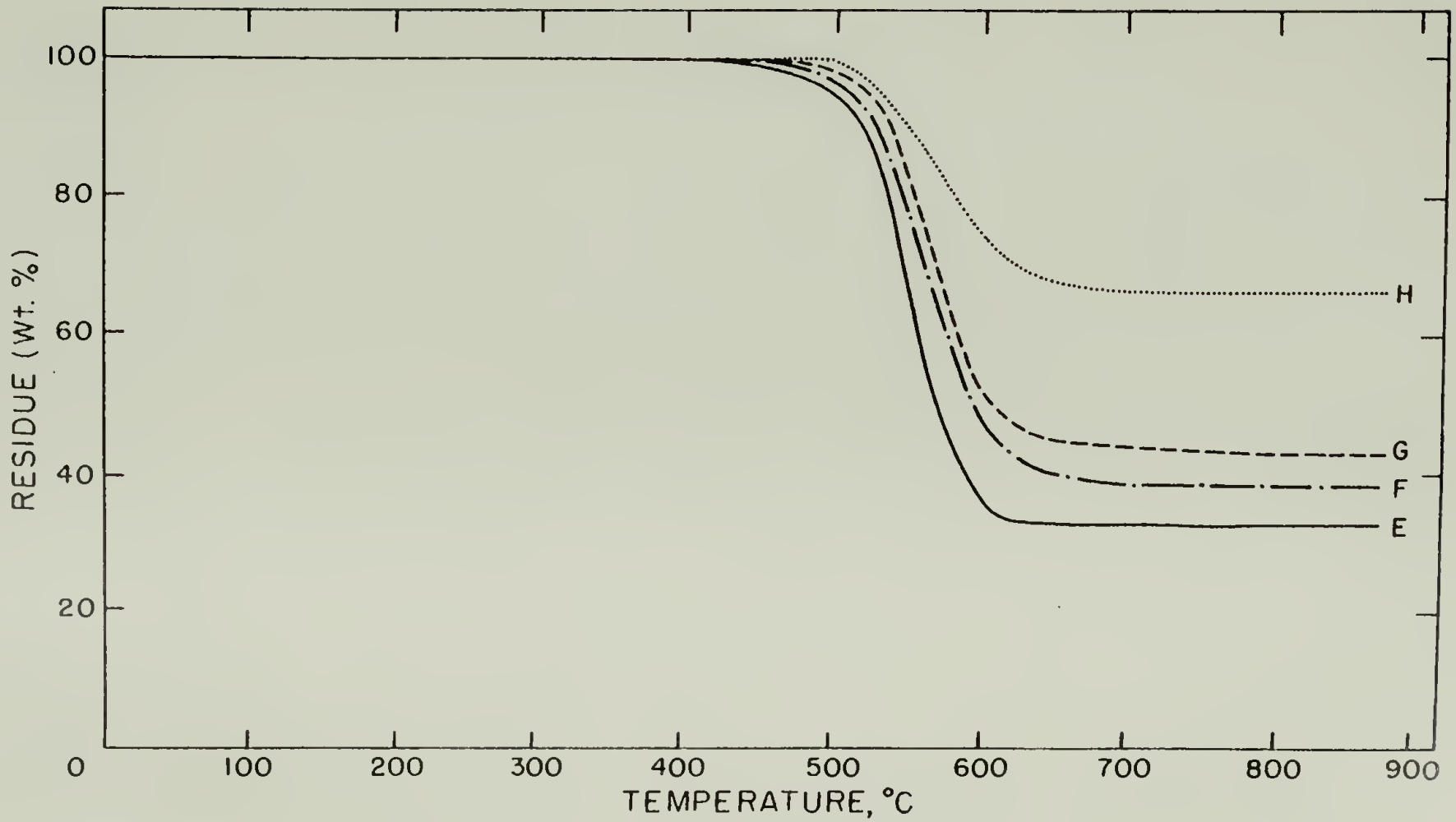


Figure 6-9. TGA in nitrogen for ether-diol silarylene-siloxane polymers containing the following amount of methylvinylsiloxane units: E: 0%; F: 5%; G: 7.5%; H: 100%.

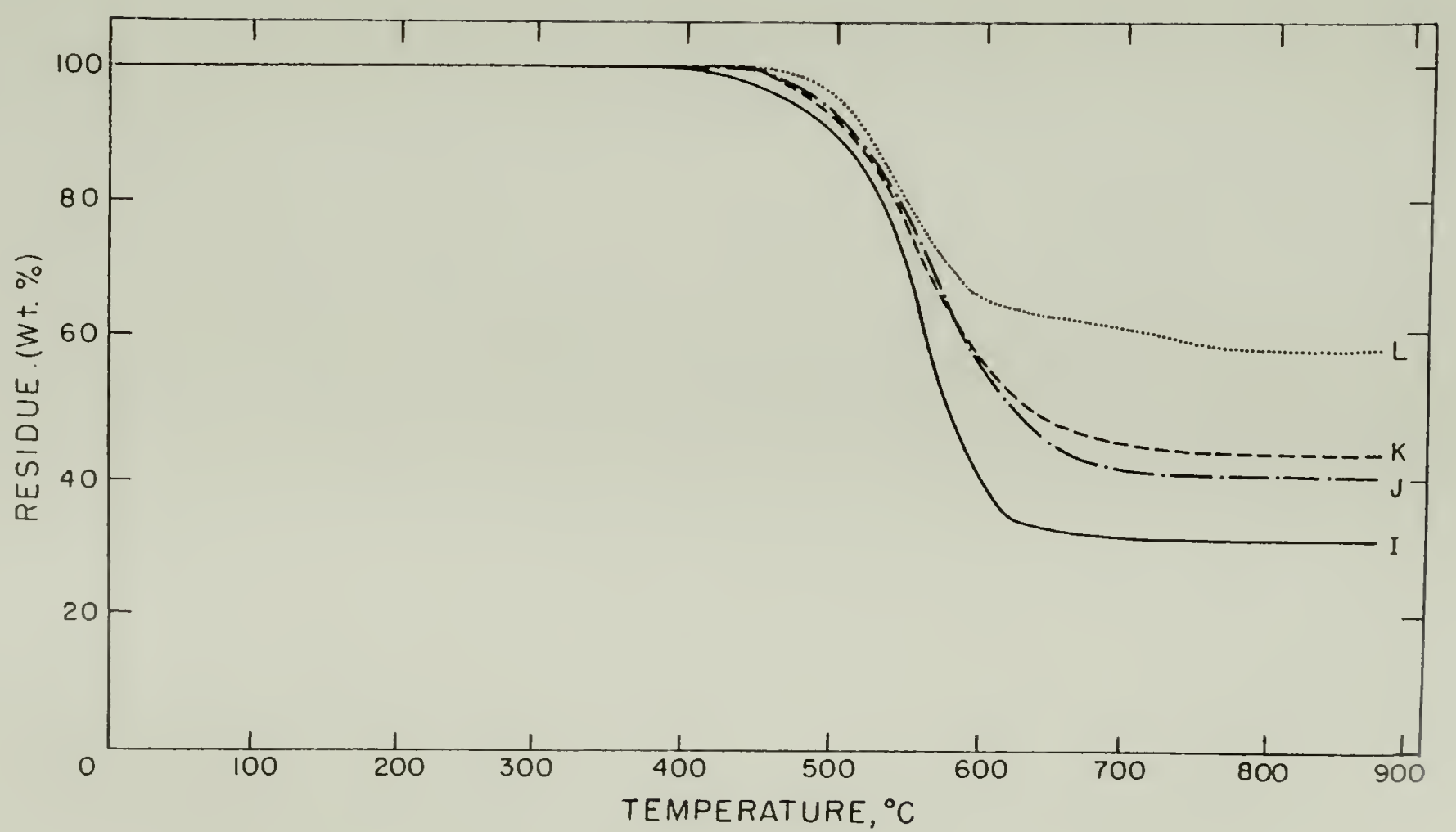


Figure 6-10. TGA in nitrogen for the silarylene-siloxane polymers prepared from a 50 mole % mixture of the two disilanols and containing the following amount of methylvinylsiloxane units: I: 0%; J: 5%; K: 7.5%; L: 100%.

TABLE 6-3

Three Steps of Degradation in Air of Exactly Alternating Silarylene-Siloxane Polymers

Polymer	First Step, wt. loss, %	Second Step wt. loss, %	Third Step wt. loss, %	Wt. remainined %
A	4.6	38.6	17.3	39.5
B	4.9	32.2	16.9	46
C	4.8	25.0	20.7	49.5
D	3.2	12.0	26.3	58.5
E	4.8	39.0	29.7	26.5
F	4.8	35.0	28.2	32
G	4.9	34.4	25.7	35
H	4.8	19.1	35.1	41
I	3.0	39.6	20.4	37
J	4.8	36.8	17.9	40.5
K	4.0	23.8	30.2	42
L	2.0	22.4	29.6	46

major losses occurred during the second and third step and their magnitudes seemed to be influenced by the content of vinyl groups present in the polymer. In the second step the amount of volatiles apparently decreased with increasing vinyl content while the situation was reversed in the third step.

(7) Elemental analysis showed that the the first step of the degradation in air (up to 450°C) was characterized by about a 20% decrease in carbon content, a very small decrease in hydrogen (not more than 5% of the original content) and a significant gain of oxygen (the originally present amount of oxygen was roughly doubled). This behavior was observed in polymers from the p-diol monomer as well as in polymers from ether-diol monomer, and it was most probably due to the splitting off of $-CH_3$ groups and establishment of crosslinks through oxygen bridges.

(8) In the second step of the thermal degradation in air, both types of alternating silarylene-siloxane polymers lost about 50% of the carbon and about 50% of the hydrogen that was left over after the completion of the first degradation step. This second step, which was in all cases completed at temperatures of about 600-620°C, was also characterized by losses of silicon and oxygen. These varied from the p-diol to ether-diol polymers, so that while Polymer A lost about 40% of Si and about 10% of O which remained after the first step, the corresponding losses in Polymer E were 20% in Si and 35% in O. This result most probably indicates that volatile organosilicon degradation products formed.

(9) The third step of thermooxidative degradation was characterized in all cases by complete annihilation of the remaining organic content. While the amount of silicon did not change during this third step there was some gain in the oxygen content. This gain ended at temperatures above 720°C to leave pure SiO_2 as the final degradation product.
(10) Finally, comparing the results from Table 6-2 with the behavior of polydimethylsiloxane under the same heating conditions (see Figure 1-8), the significantly higher thermal stability of the exactly alternating silarylene-siloxane polymers compared to a polysiloxane homopolymer can be seen in Table 6-4.

In an attempt to learn more about the degradation of the exactly alternating silarylene-siloxane polymers, elemental analysis of the degradation products were obtained. The results for representative polymers are presented and compared with the elemental composition of original polymers in Table 6-5. It can be seen from this Table that:
(1) During the degradation in nitrogen the differences in carbon content between the original polymers and degradation products were never larger than 10%.
(2) Changes in the silicon content were even smaller (3-4%) and proceeded in the opposite direction.
(3) Even after heating the samples in a nitrogen atmosphere up to 960°C, there was still 1-2% of hydrogen left in the degradation products.
(4) The degradation products appeared black and were insoluble in many of the commonly used solvents (tetrahydrofuran, chloroform, acetone,

TABLE 6-4

Comparison of Degradation Behavior in Nitrogen[a] of Poly(dimethylsiloxane) and Exactly Alternating Silarylene-Siloxane Polymers: A, E and I

Polymer	Disilanol	Onset of degrad., °C	Temp. for 50% weight loss, °C	End of degrad., °C	Wt. remained, %
Poly(dimethylsiloxane)[b]		290	445	600	25
A	p-diol	400	545	660	30.5
E	ether-diol	410	520	650	33
I	50 mole % mixture	390	530	750	31.5

[a]Measured at a heating rate of 15°C/min.

[b]As reported by Pittman and coworkers(3)

TABLE 6-5

Comparison Between the Elemental Compositions of Degradation Products[a] and Original Polymers

Polymer	Original Polymers				Degradation Products			
					in N_2[b]			in air[c]
	%C	%Si	%H	%O	%C	%Si	%H	%Si[d]
A	50.2	30.0	8.4	11.5	41.8	27.4	1.3	45.5
D	52.0	28.7	7.3	12.1	41.5	30.1	1.3	44.8
E	56.0	23.1	6.8	14.1	44.0	25.0	-	48.0
G	57.6	22.9	7.0	12.5	48.0	26.0	-	47.0
H	59.4	21.7	6.7	12.2	47.0	25.0	-	47.0
I	54.9	25.3	7.6	12.2	50.0	28.7	1.7	42.0

(a) All the products were heated to 960°C.

(b) No detectable amounts of nitrogen could be found in any of the samples.

(c) No detectable amounts of carbon could be found in any of the samples.

(d) %Si in SiO_2 is 46.7.

benzene, toluene).

(5) During the degradation in air the polymers lost all of their organic groups and silicon dioxide remained in all cases as the final product at temperatures above 730°C.

C. Pyrolysis of Exactly Alternating Silarylene-Siloxane Polymers

In order to learn about the products of the thermal degradation of exactly alternating silarylene-siloxane polymers, two representative samples, Polymers A and E, were pyrolysed in a helium atmosphere. A Chromalytics Multi-Purpose Thermal Analyzer, Model MP-3, in line with Varian Gas Chromatograph, Model 2700, was used for this purpose. The samples were heated from 200 to 800°C at a heating rate of 16 and 40°C/min. The degradation products were trapped on Tenax-GC cooled to liquid nitrogen temperature and then back-flashed into gas chromatograph. For GC separation a Carbowax 20 M stainless steel column was used and the chromatograms are recorded during the programmed heating of the column from 30 to 215°C at heating rate of 10°C/min.

A typical thermogram obtained for Polymer A showing the relative amounts of volatile products formed as a function of temperature is given in Figure 6-11. The GC chromatograms obtained for the products of decomposition of Polymers A and E are shown in Figures 6-12 and 6-13, respectively.

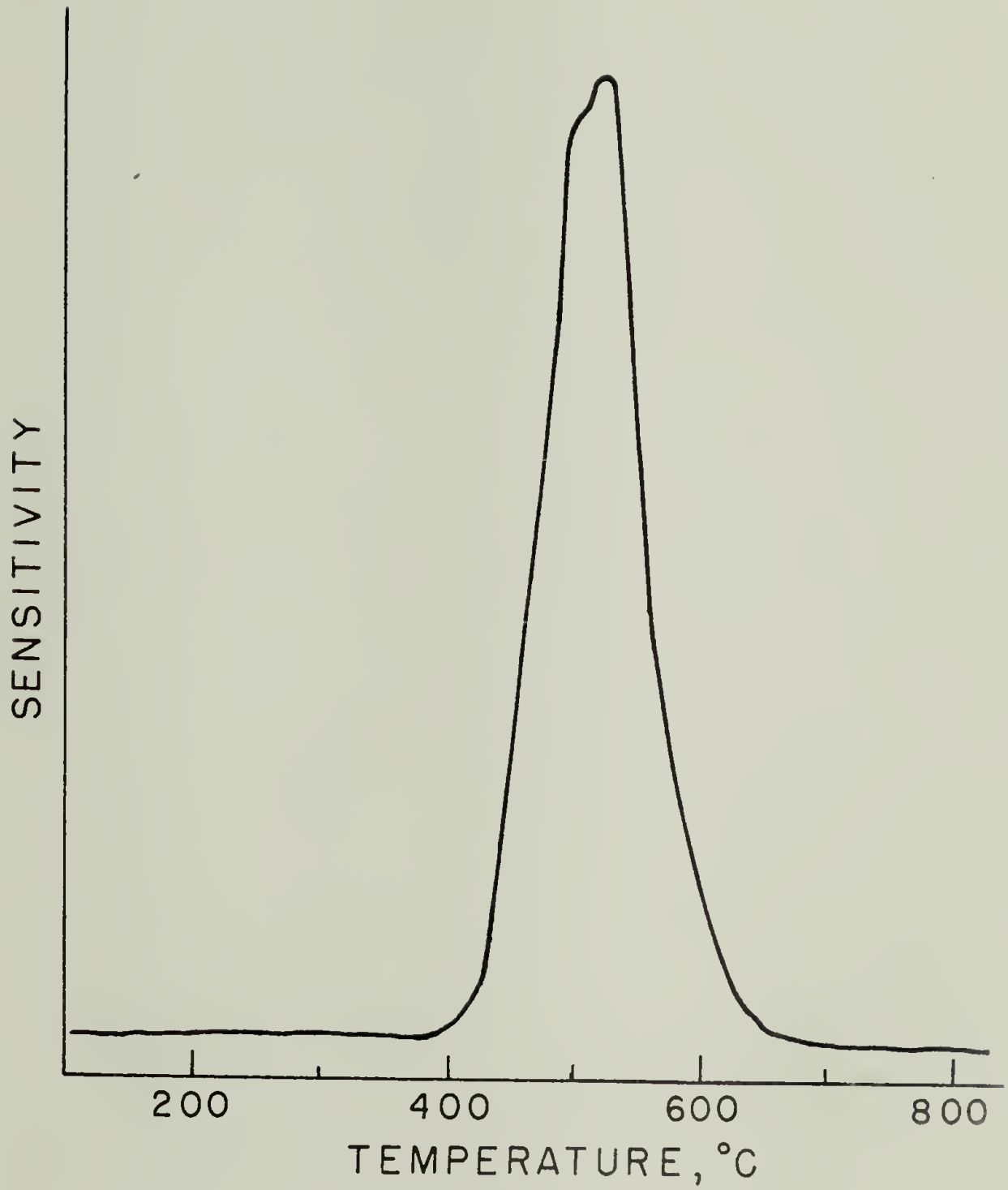


Figure 6-11. Formation of volatile degradation products during the pyrolysis of Polymer A.

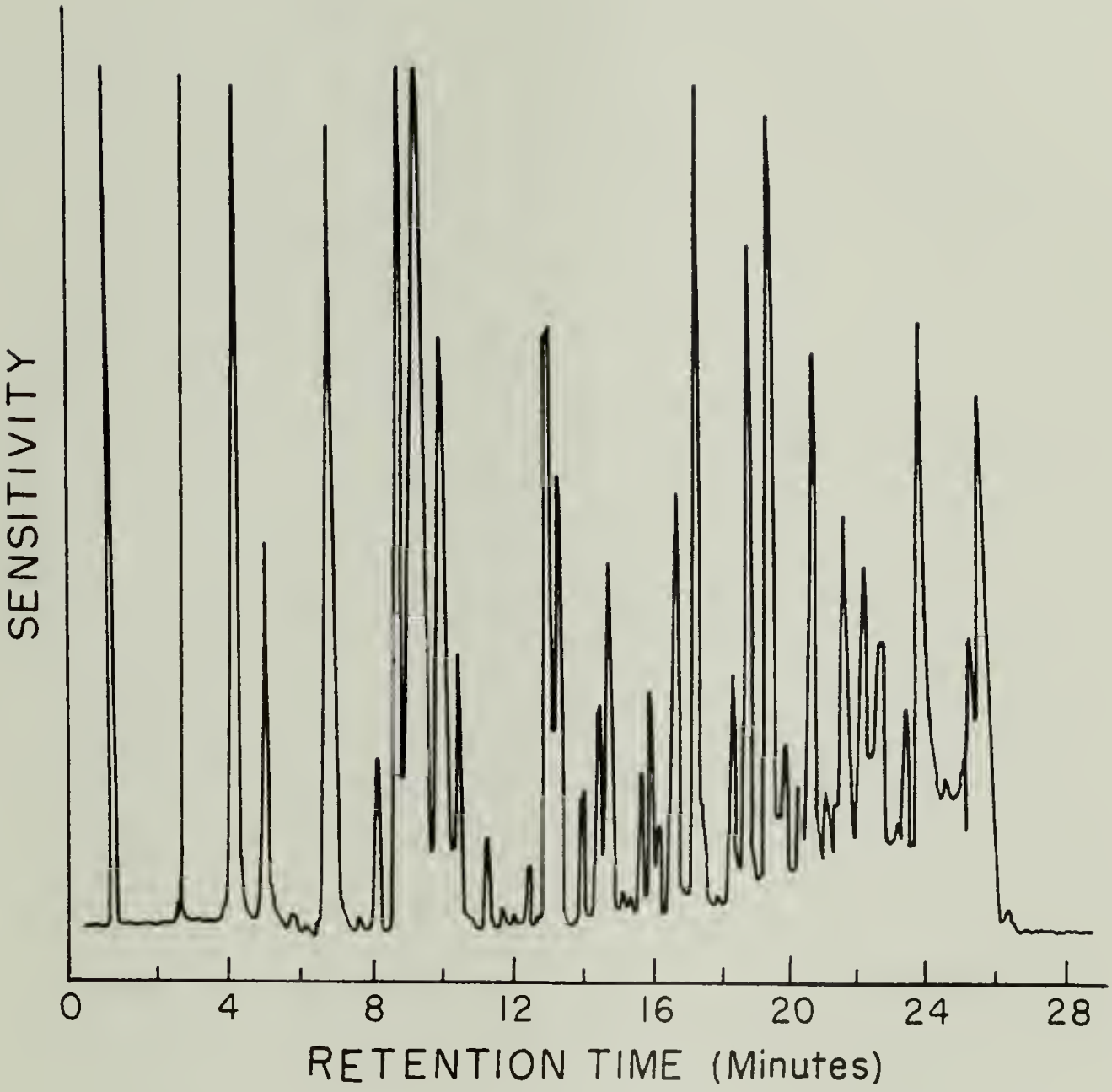


Figure 6-12. Gas chromatogram of the trapped volatile products of the pyrolysis of Polymer A.

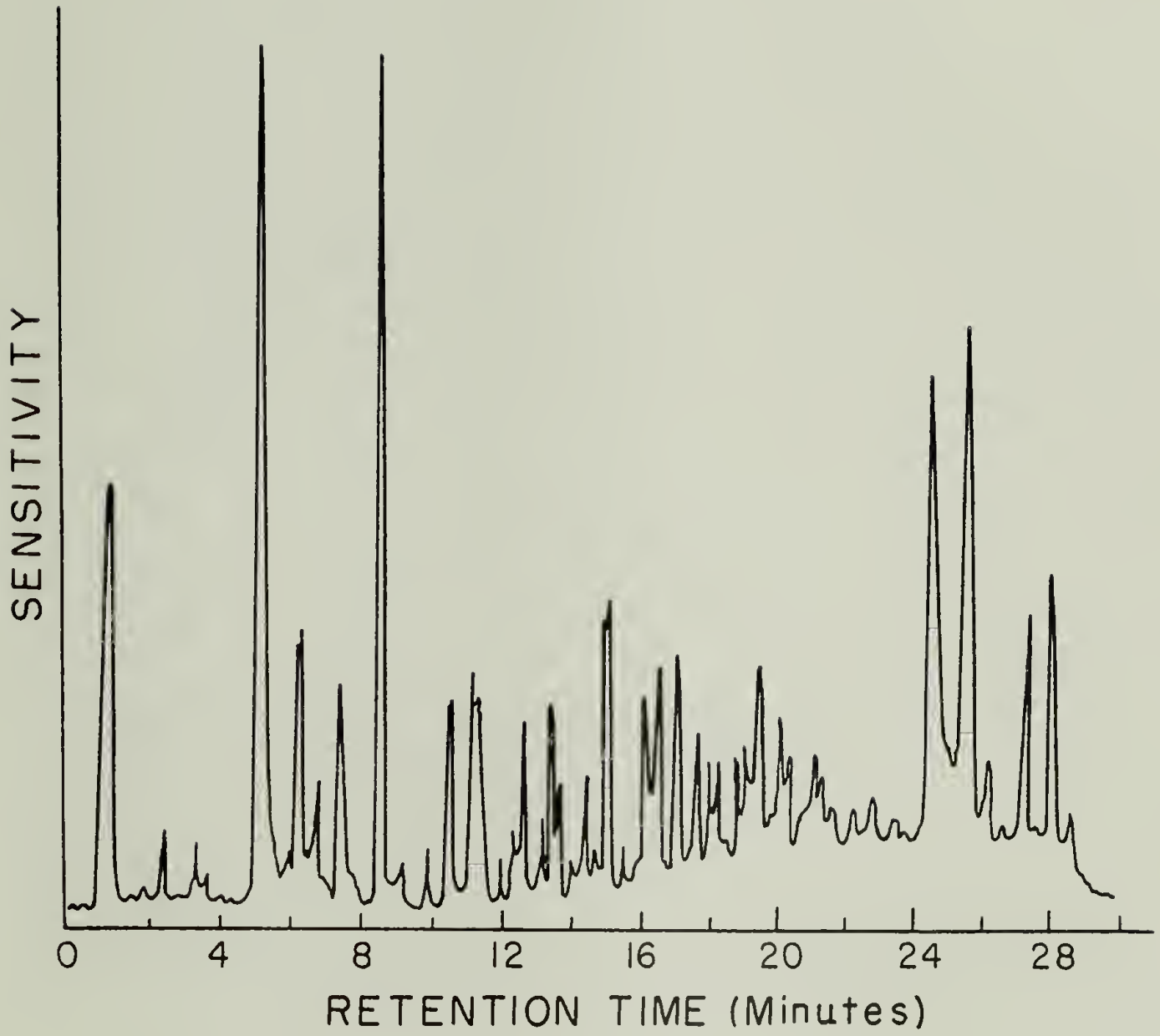


Figure 6-13. Gas chromatogram of the trapped volatile products of the pyrolysis of Polymer E.

It can be seen from these results that:

(1) The pyrolysis thermogram (Figure 6-11) correlated very well with the TGA thermogram for the same Polymer A (Figure 6-6). In both cases, the degradation started at 400°C and ended at about 650°C. The maximum rate of the production of volatiles was achieved at 520°C (Figure 6-11), which was about 25°C below the temperature at which 50% of the weight was lost (Table 6-2), but it correlated very well with the inflexion point in the TGA thermogram (Figure 6-6). This probably indicates that the mechanisms of thermal degradation were the same in nitrogen and helium stmosphere.

(2) The results obtained by GC analysis indicated that there was a large number of volatile products formed during the thermal degradation of these polymers, and it depended on the heating rate. Comparing Figures 6-12 and 6-13 it seems that faster heating rates resulted in fewer volatile products so that about 15 major products were formed and separated during the degradation of Polymer A at 16°C/min, while their number was reduced to about 5 for degradation of Polymer E at 40°C/min.

(3) Although silicones, and even more so, silarylene-siloxanes, are among the most thermally and oxidatively stable polymers known, there has been no systematic study of their degradation mechanism reported as yet. These preliminary experiements seem to indicate that such a study would be a very interesting one, and it could eventaully lead to a much better understanding of what makes these materials so thermally stable, as well as to possible identification of the degradation mechanisms.

Bibliography

1. K.A. Andrianov, "Metalorganic Polymers", Interscience, New York (1965), p. 48-70.

2. E.A. Collins, J. Bares, F.W. Billmeyer, Jr., "Experiments in Polymer Science", Interscience, New York (1973), p. 252.

3. C.U. Pittman, Jr., W.J. Patterson, S.P. McManus, "Oxysilane Polymers from Silanediol-Bisdimethylaminosilane Polycondensations: Synthesis and Properties", J. Polymer Sci., Polymer Chem. Ed., 14, 1715 (1976).

C H A P T E R V I I

SUGGESTIONS FOR FUTURE WORK

Although it may be considered that the main goal of this work, which was preparation and evaluation of exactly alternating silarylene-siloxane polymers, has been successfully accomplished, in the course of these investigations, as is usual in scientific research, many new interesting possibilities and problems were uncovered.

A number of different vinyl containing linear copolymers have been prepared. It will be necessary to optimize the vulcanization procedures of these by utilizing their vinyl groups as potential cross-linking sites in reactions with different organic peroxides such as benzoyl or dicumyl peroxide before it is possible to investigate their mechanical properties. For these purposes, the samples studied should be either cast or compression-molded films, which would be cross-linked after film formation.

Most of the existing siloxane polymers are known to have relatively small viscosity-temperature coefficients. It would be interesting to find out how the introduction of different silarylene groups influences this property. Thus, measurements of the dynamic mechanical properties and the rheological properties of the linear as well as the cross-linked polymers would be desirable. These measurements should be carried out over the broad temperature range, from approximately -100°C to 350°C.

The condensation polymerization reaction developed in this work, and discussed in detail in Chapter IV, permitted the use of a wide variety of reaction conditions and monomers. It would be most interesting to reinvestigate possibilities for successful preparation of 1,3-(dimethylhydroxysilyl)benzene and 4,4'-bis(dimethylhydroxysilyl) diphenyl dimethylsilane monomers and use them to prepare a series of polymers analogous to those prepared here from the p-diol and ether-diol monomers. These polymers could be expected to show even better low temperature properties while retaining high thermal stabilities comparable to those of the polymers prepared in this work.

The other possible monomers of interest would be new bisureidosilanes. Especially promising among these, from the polymer properties viewpoint, would be derivatives with longer alkyl groups attached to the silicon atom, as well as with fluorinated alkyl groups. This suggestion is based upon the observed internal plasticizing effect of the vinyl groups in polymers prepared in this work, which may become even more pronounced in polymers with larger groups pendant to the main chain and, consequently, may lead to an even larger decrease in the T_g value.

Another area which would certainly warrant study is an investigation of the mechanism of the thermal degradations of silarylene-siloxane polymers in both nitrogen and air. The results of the investigations in this area, described in Chapter VI, seem only to touch on the subject. These preliminary results indicate a remarkable degree of inherent thermal stability in these polymers, but also a high degree of

complexity of the degradation. By determining the IR spectra, molecular weights and mass spectrometric characteristics of the volatile products of thermal degradations of these polymers the mechanism of the process could be elucidated to add new knowledge about degradation and stability of high polymers in general and of these extremely thermally-stable polymers in particular.

Finally, a study of the long-term isothermal degradation of the linear and cross-linked polymers, to determine weight-loss behavior and the effect of extended high temperature exposure on the mechanical properties, would be desirable.

APPENDIX

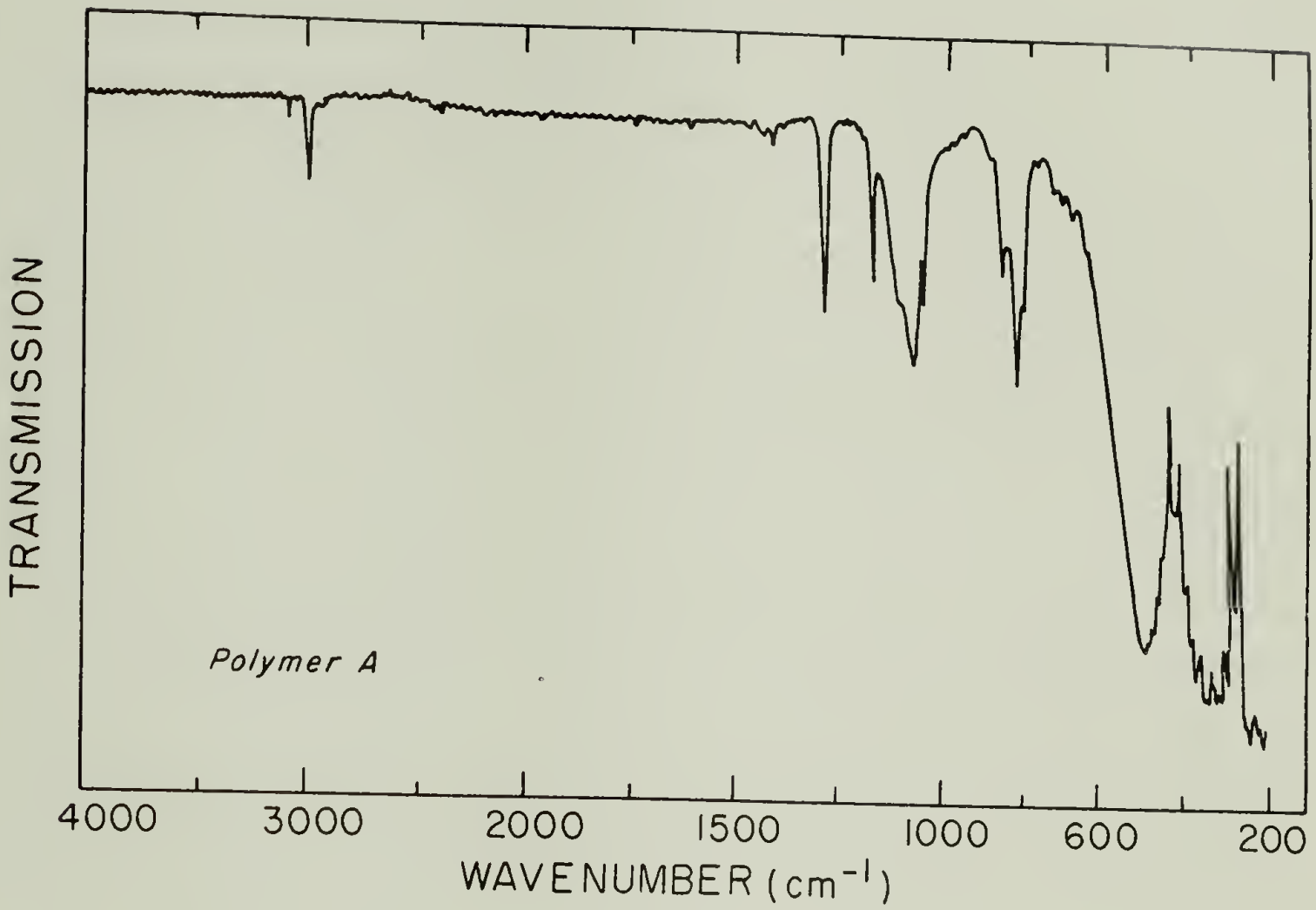


Figure 8-1. IR spectrum of Polymer A.

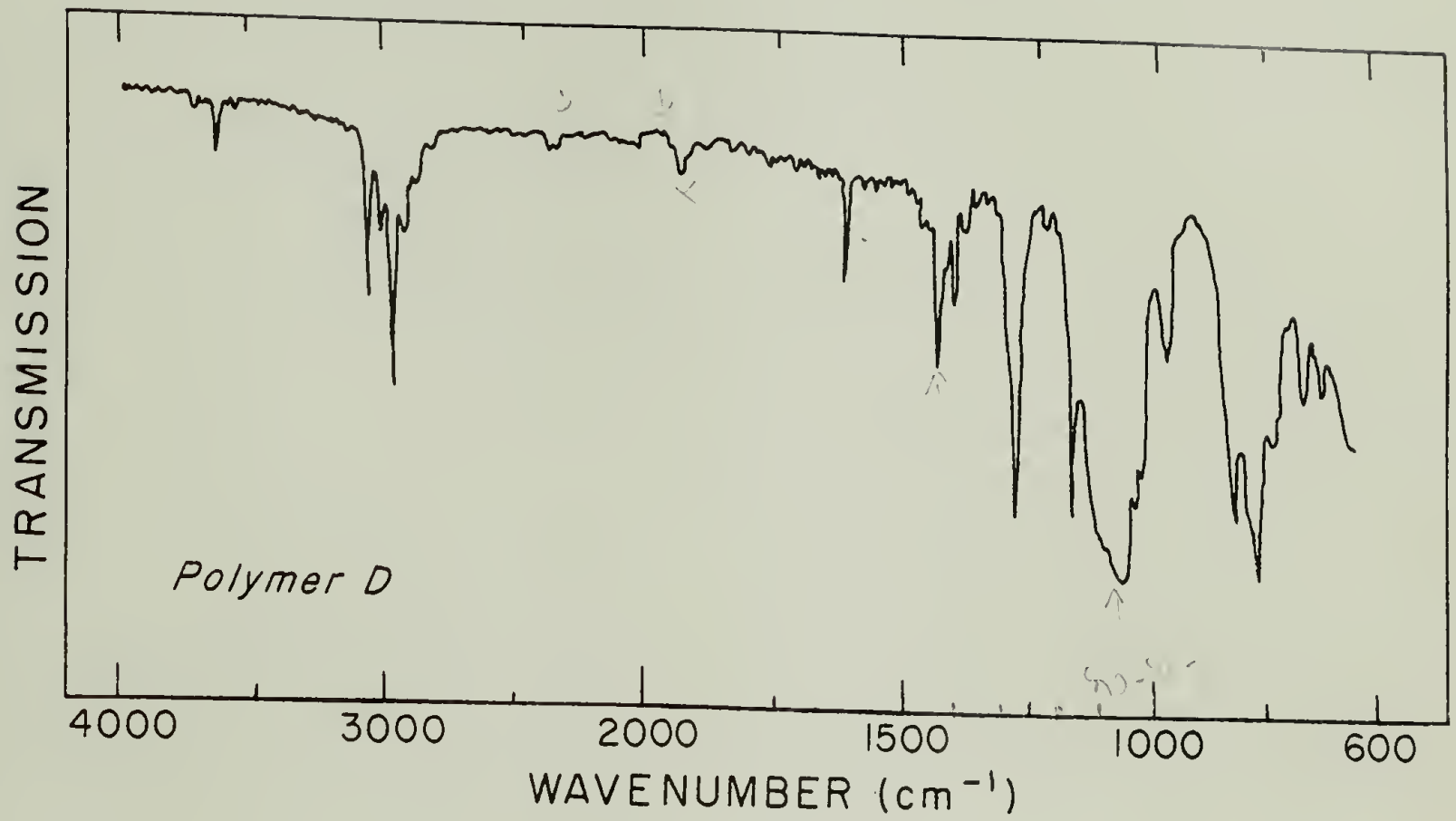


Figure 8-2. IR spectrum of Polymer D.

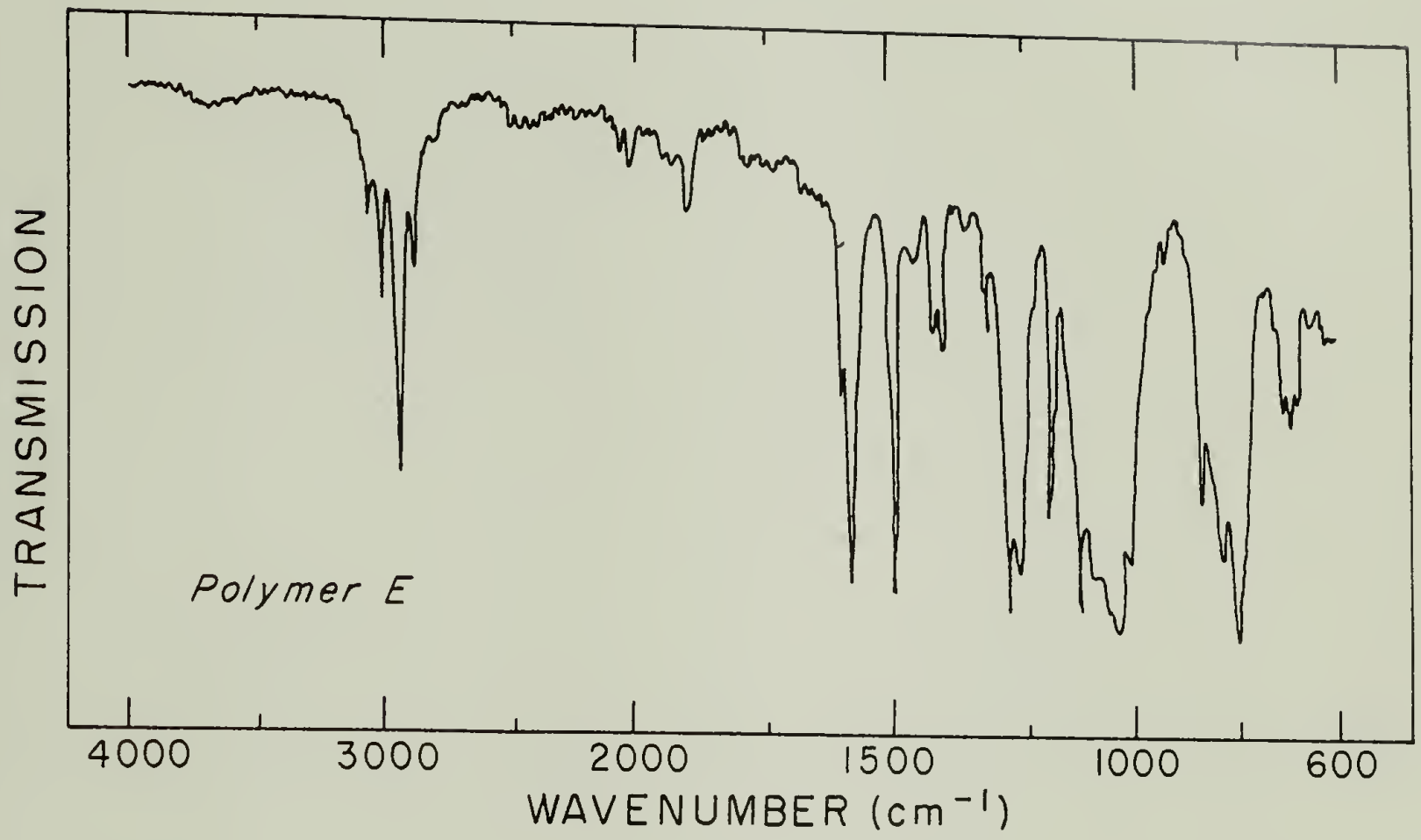


Figure 8-3. IR spectrum of Polymer E.

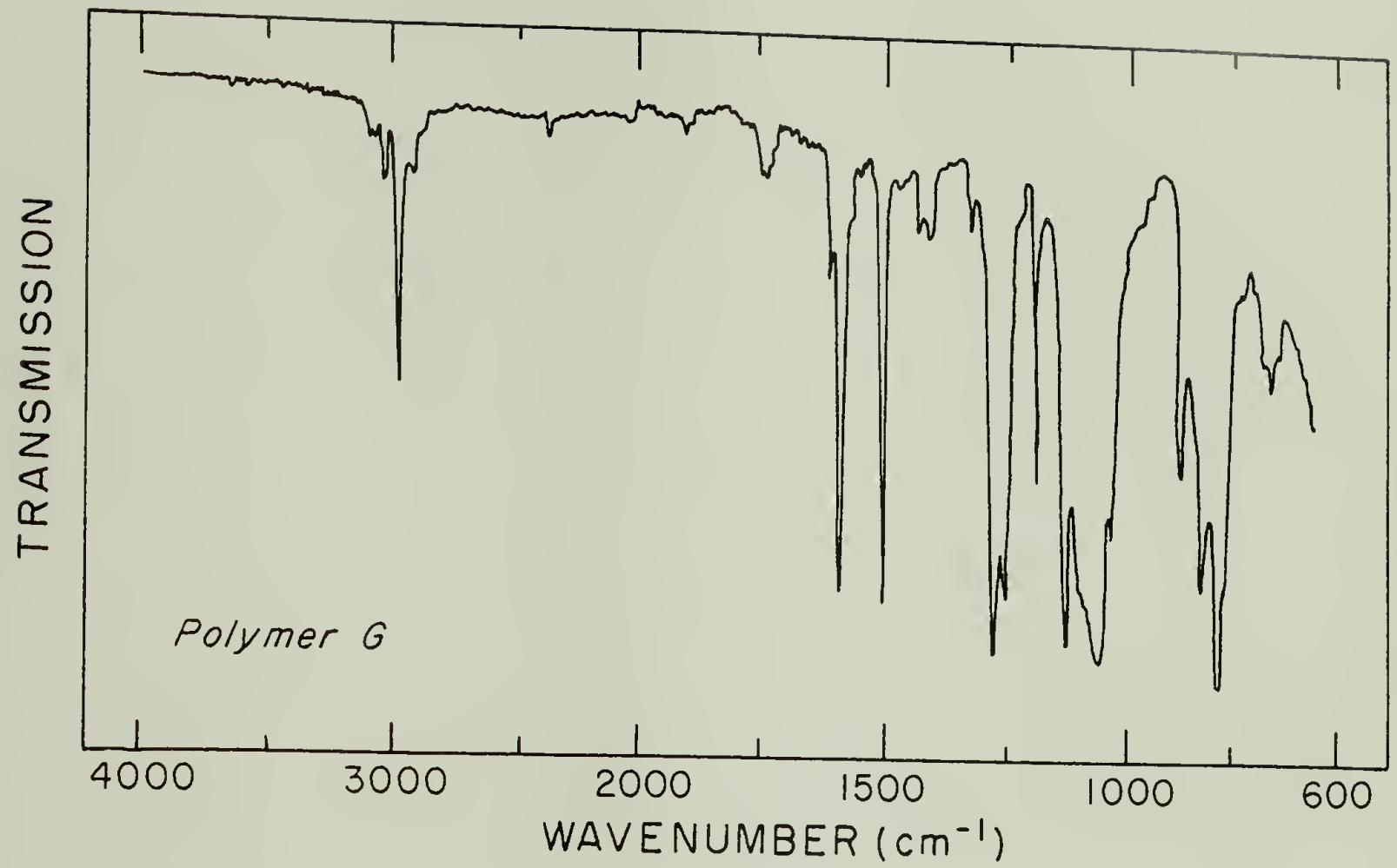


Figure 8-4. IR spectrum of Polymer G.

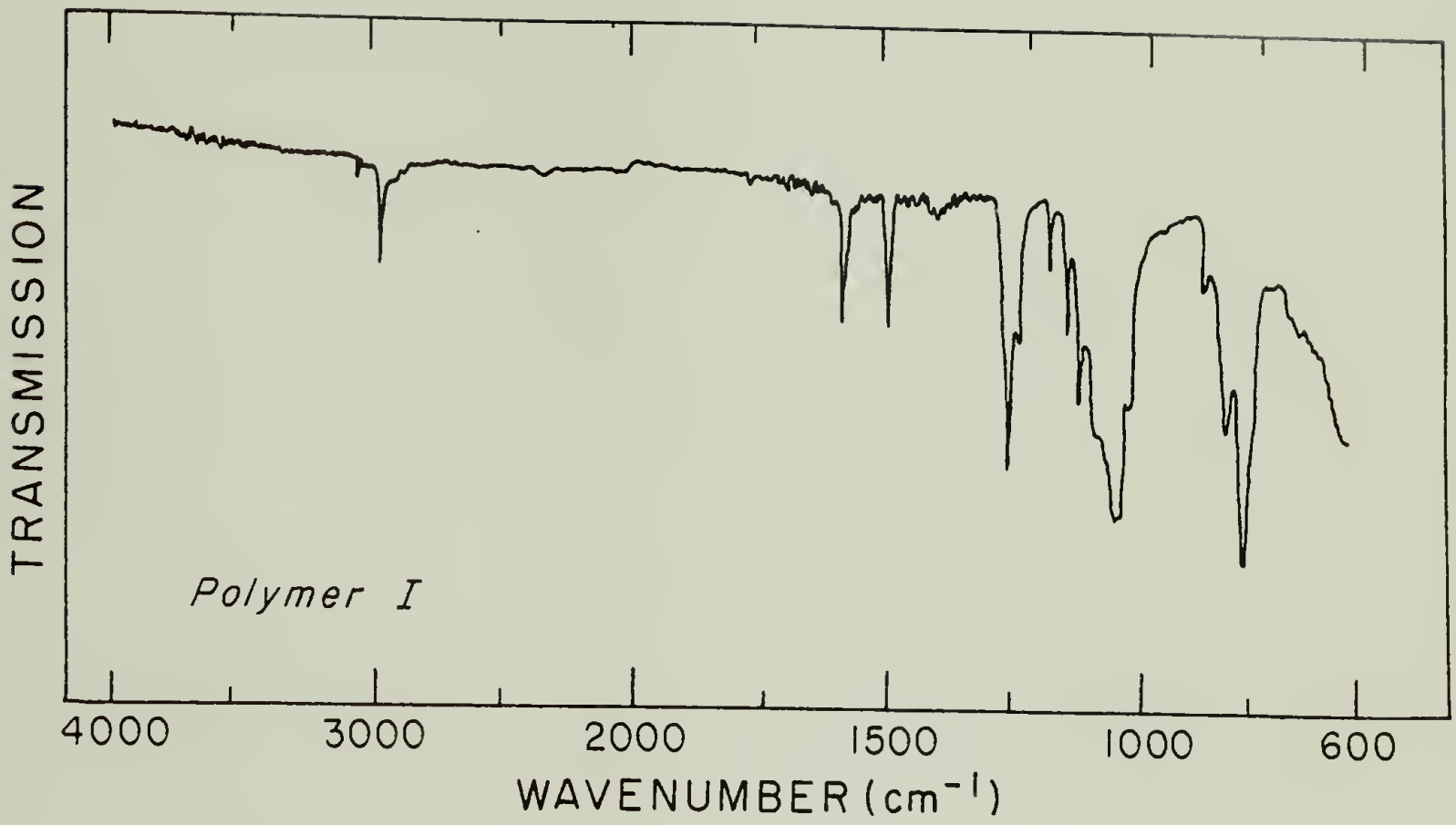


Figure 8-5. IR spectrum of Polymer I.

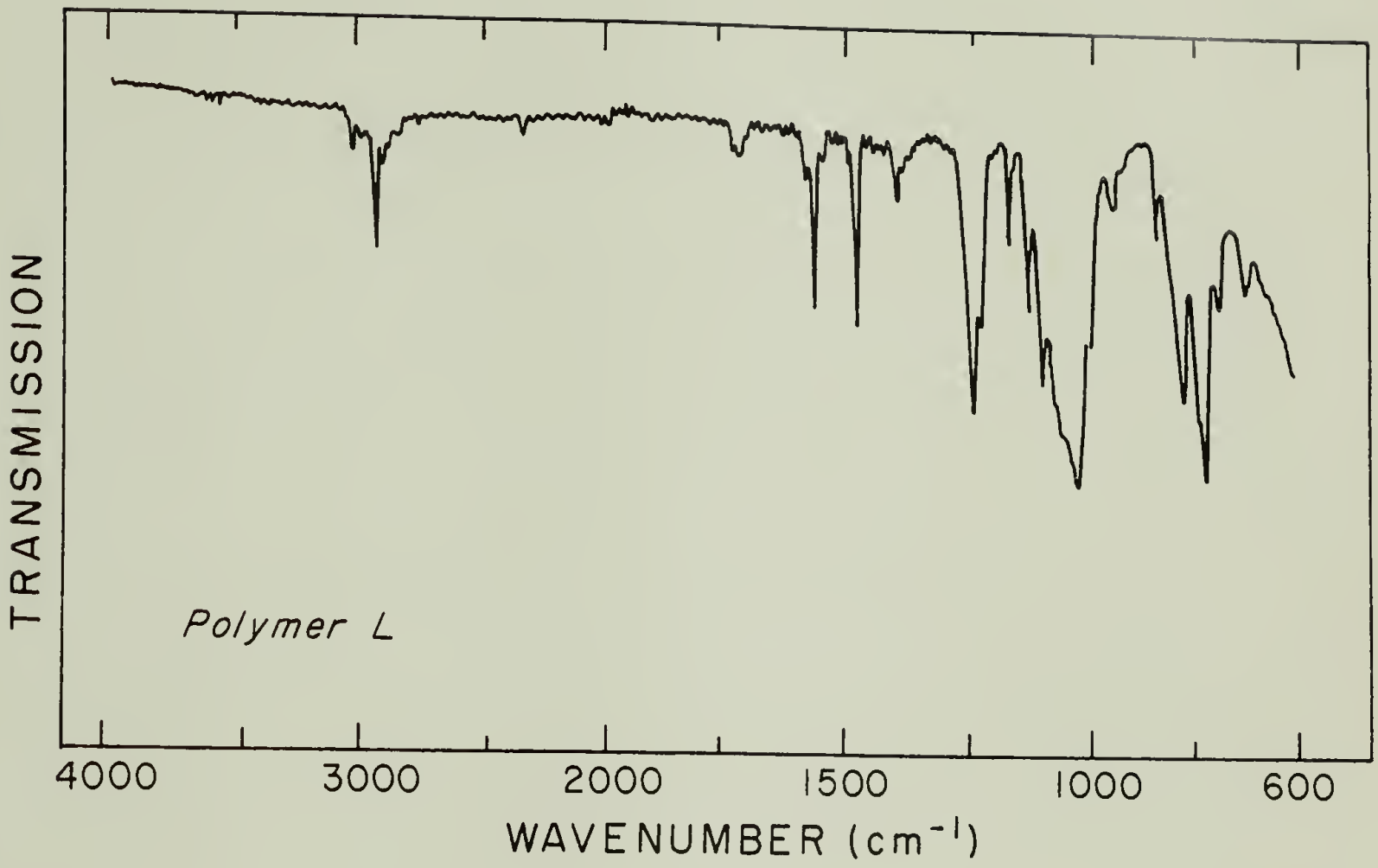


Figure 8-6. IR spectrum of Polymer L.